

Reducing carbon-in-ash

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Abstract

High levels of carbon-in-ash cause difficulties for power plant operators. It leads to reduced overall plant efficiency and higher fuel costs, degrades the performance of electrostatic precipitators and leads to increased emissions of particulates. Increased carbon levels in the fly ash can lead to problems with ash use in cement/concrete production, the most profitable and largest ash utilisation option. This report reviews current measures and technologies that can be used to prevent excessive carbon-in-ash in pulverised coal combustion (PCC) power plants. These include coal cleaning, coal fineness improvement, reduction of distribution imbalance of coal among burners, increasing coal-air mixing rates at both burner and OFA levels and optimising excess air ratios. A plasma-assisted combustion enhancement technology can help achieve better ignition and more stable flame for coals that are normally difficult to burn. Computer-based combustion optimisation using expert systems, neural network systems and coal combustion simulation is becoming an invaluable means to tackle the carbon-in-ash issue. This report also reviews the regulations in nine major coal-consuming countries, which stipulate the maximum unburnt carbon levels permitted for fly ash for use in concrete/cement production. The Loss on Ignition (LOI) parameter is used in all national standards, although it is considered inadequate and may exclude some usable fly ash from being utilised. Performance-based regulations are more appropriate and have been adopted by Canada and USA. The EU and Canada now permit the use of fly ash produced from co-combustion of coal and biomass although its dosage is limited. Apart from China and Russia where very high LOI levels are allowed for certain fly ash, the other countries require similar LOI limits for fly ash for use in concrete. Finally, this report discusses measures and technologies for reduction of carbon-in-ash, including classification, froth flotation, triboelectrostatic separators, thermal processes (combustion, fusion or steam gasification), and carbon surface modification.

Acronyms and abbreviations

AASHTO	American Association of State Highway and Transportation Officials	PECOSTM	plant environmental and cost optimisation system
ACAA	American Coal Ash Association	PFBC	pressurised fluidised bed combustion
ADAA	Ash Development Association of Australia	PFS	plasma fuel system
AEA	air entrainment admixture	PLC	programmable logic controller
AI	abrasive index	PRB	Power River Basin (USA)
ASR	alkali silicate reaction	REACH	registration, authorisation, evaluation, restriction of chemicals
ASTM	American Society for Testing and Materials	RMI	reactive maceral index
BIS	Bureau of Indian Standardisation	SCM	supplementary cementitious material
BRI	bimaceral reflectance index	SA	secondary air
CBASTM	coal blend automation system	SCR	selective catalytic reduction
CBK	carbon burnout kinetics	SEM	Scanning Electron Microscopy
CBOTM	carbon burn-out	SNCR	selective non-catalytic reduction
CARNO	carbon-in-ash notification system	ST	Separation Technologies LLC (USA)
CCC	Clean Coal Centre (London, UK)	US DOE	US Department of Energy
CCD	charge-coupled device	US EPA	US Environmental Protection Agency
CCP	coal combustion products	USSR	Union of Soviet Socialist Republics
CFD	computational fluid dynamics		
CIRCA	Canadian Industries Recycling Coal Ash		
CPD	chemical percolation devolatilisation		
CSA	Canadian Standard Association		
CTF	coal test facility		
CSI	coal stability index		
DCS	digital control system		
DDP	4-dodecylphenol		
DTF	drop tube furnace		
DTI	Department of Trade and Industry (UK)		
ECOBA	European Coal Byproducts Association		
EDS	Energy Dispersive X-ray Spectroscopy		
ESP	electrostatic precipitator		
FACTTM	fly ash carbon treatment		
FBC	fluidised bed combustion		
FG-DVC	functional group-depolymerisation vaporisation cross-linking		
FGD	flue gas desulphurisation		
FLASHCHAIN	flash distillation-distributed energy chain statistics		
GNOCISTM	generic neural optimisation control intelligent system		
HEX	hexadecane		
HGI	Hardgrove grindability index		
IEA	International Energy Agency		
IGCC	integrated gasification combined cycle		
JIS	Japanese Industrial Standard		
LEED®	Leadership in Energy and Environmental Design (USA)		
LOI	loss on ignition		
MCB	microwave carbon burnout		
MIBC	methyl isobutyl carbinol		
NMR	nuclear magnetic resonance		
NP	nonylphenol		
OECD	Organisation for Economic Co-operation and Development		
OFA	overfire air		
PA	primary air		
PC	pulverised coal		
PCC	pulverised coal combustion		
PDF	probability density function		

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I Introduction

Coal will remain the main fuel for power generation worldwide up to and perhaps beyond 2030. Although difficulties arise in many cases in construction of new coal-fired power plants, largely because of uncertainty on climate policies and opposition driven by environmental concerns, coal-based generating capacity is actually increasing steadily. The IEA reported that a total of 31 GW is now under construction in OECD countries, on top of the 28 GW capacity that has come on line since 2000. These figures are dwarfed by the increase outside the OECD, notably in China, where the growth in coal-fired generation more than doubled between 2000 and 2006. Coal's share in the world power generation is projected to increase from 41% in 2006 to about 44% by 2030 in the IEA's reference scenario (IEA, 2008a).

In OECD countries, an average of 81% of coal consumption will be used for power generation between 2006 and 2030 (IEA, 2008a). Coal use on such a grand scale produces enormous amounts of fly ash, which is the largest 'waste' stream from coal-fired power plants (Punshon and others, 2003). Conventionally fly ash has been landfilled near to its producing plant but such disposal can lead to environmental pollution. The utilisation of coal fly ash in an environmentally acceptable manner is preferable to disposal underground. Tightened environmental regulations are also making landfill of fly ash more costly. If a proportion of the produced fly ash can be utilised beneficially, power plant operators can not only reduce their annual landfill cost and lengthen the lifetime of available ash ponds, but also generate a considerable income from ash sales.

There are generally two reasons for excessive unburnt carbon in fly ash. The first is that low NO_x systems, installed in order for a plant to comply with more stringent NO_x emission regulations, may unfortunately impact on the burnout performance of coal particles (DTI, 1999; Hower and others, 1999; Wu, 2002). The second reason lies with plant operators who want to reduce fuel costs or increase fuel supply security by purchasing and using cheaper coals in their power plants. Burning unfamiliar coals often necessitates modifications to operating conditions to maintain safe and stable plant operation. Changes in either fuel properties or operating conditions may cause difficulties in coal combustion, leading to increased carbon-in-ash (Skorupska, 1993).

Excessive carbon-in-ash is undesirable. The most important reason is that the marketability of boiler ash is reduced (*see* Chapter 3). Excessive unburnt carbon also represents an obvious fuel loss, thus impairing other efforts to improve overall plant efficiency. Moreover, the efficiency of electrostatic precipitators (ESP) can be reduced if fly ash contains too much unburnt carbon (Elston, 2003; Colechin, 2004). This is because carbon can lose its electrical charge very quickly due to its high conductivity, and so re-enter the gas stream from an ESP's collecting plates. Consequently the stack opacity can increase considerably, which is a significant issue considering the strict particulate emission limits that a plant has to comply with. With an increase of carbon-in-ash

and a reduction of ESP efficiency, the amount of black carbon emitted to the atmosphere from the stack increases. Black carbon is increasingly being recognised as a major short-lived contributor to global warming (US EPA, 2008). Excessive carbon in ash is a safety hazard as well. It can, and has, caused explosions in ESP and fly ash silos for temporary storage of ash at power plants.

This report discusses the carbon-in-ash issue with pulverised coal combustion (PCC) units only. PCC units currently account for approximately 98% of the total electricity produced from coal (Wu, 2003). The total capacity of fluidised bed combustion (FBC) units is much smaller than that of PCC units. Moreover, little FBC ash is actually used in the production of cement/concrete. Coal gasification based generation units are also excluded from this report for the reason that only eight operating units (1.98 GW capacity in total) exist worldwide (GTC, 2009). Consequently, only a limited quantity of ash and slag is produced, which is mostly used in low-value applications such as road-base materials. It is also easy to find alternative materials for these low-value applications.

This report starts with a discussion of measures available to prevent excessive carbon-in-ash, then discusses regulations relevant to fly ash use in cement/concrete production in major coal-using countries, and finally introduces the various carbon-in-ash reduction technologies currently available.

Formation of carbon-in-ash is reviewed in Chapter 2, with an emphasis on factors affecting the burnout of coal particles. These factors include coal types, coal particle fineness, firing pattern, air-fuel ratio and combustion conditions. Chapter 3 describes, based on consideration of the above factors, measures available to improve the coal burnout in the furnace, including coal cleaning, improvement in coal fineness, coal selection and blending, and various ways to optimise coal combustion.

The impact of excessive carbon-in-ash on ash utilisation is discussed in Chapter 4. The present status of regulations concerning the carbon-in-ash permitted for ash utilisation in major coal-using countries is reviewed.

Measures already commercially available or under development to reduce carbon-in-ash are discussed in Chapter 5. The operational principles and large-scale trials of each measure are introduced when such information is available from the public literature. In addition, the fate of ammonia and mercury, adsorbed on ash as a result of emissions control, during carbon reduction processes is also discussed in Chapter 6.

This report complements three earlier IEA Clean Coal Centre reports on the utilisation of coal ash from PCC boilers, FBC boilers and IGCC plants (Sloss, 1999; Adams, 2004; Smith, 2005).

2 Formation of carbon-in-ash

The immediate solution to prevent excessive carbon-in-ash is to improve the coal burnout in PCC boilers. A better understanding of the combustion behaviour of pulverised coal in full-scale PCC boilers is necessary to achieve this. Fundamental principles of pulverised coal combustion have been reviewed recently by Wu (2005). This chapter briefly reviews these principles with an emphasis on factors affecting coal burnout. The greatest challenge is to achieve low NO_x emissions with high coal burnout.

2.1 Pulverised coal combustion

Pulverised coal (PC) firing differs from the other coal combustion technologies primarily in the much smaller particle size used and the resulting high combustion rates. Nominal diameters of typical pulverised coal are in the range of 5–400 µm; for a bituminous coal, 70–75% of particles are below 75 µm, with less than 2% of particles over 300 µm. Under pulverised coal firing conditions, the heating rate of coal particles is high, of the order of 1×10^5 °C/s. Due to its small size (and therefore large specific surface area) and high heating rate, a pulverised coal particle can completely burn out in approximately 1–2 seconds.

Coal pulverisation takes place in coal pulverisers or mills. Heated primary air (PA) is used to transport coal into and out of pulverisers through to burners, and to dry the coal. The quantity and temperature of PA varies significantly with the type of pulveriser, grinding rate and coal properties. Secondary air (SA) is introduced through a burner to the PA/PC mixture, in a controlled manner to induce air-fuel mixing in the furnace. As a coal particle enters the furnace, its surface temperature increases due to radiative and convective (though less important) heat transfer from furnace gases and other burning particles. The remaining moisture is vaporised and the organic mass of coal begins to decompose. Some decomposed fractions of coal organic mass can evolve as volatile matter which includes both light hydrocarbon gases and tars. Tar is a heavy hydrocarbon-like substance with an atomic H/C ratio greater than 1.0 (Wu, 2005). The volatile matter ignites and burns almost immediately and further raises the temperature of the remaining solid coal mass (termed char). Volatile combustion is a rapid process, generally completed within a few milliseconds, whereas char oxidation reactions are much slower, in the order of seconds (Sami and others, 2001). This is because oxygen must be transported to the surface of char particles, which is a slower diffusion process than gas-phase mixing of volatiles with air. Char combustion thus determines the coal combustion rate and hence burnout. Moreover, the volatile flame is generally somewhat away from the char surface due to the volatile escape velocity. The distance between the char particle and the gas-phase flame gradually reduces as the devolatilisation reaction slows down. Therefore, volatile combustion has negligible effects on the combustion of char. However, the volatile combustion rate is important with respect to formation of pollutants (Sami and others, 2001).

In spite of many research efforts, the complex mechanism of char combustion is still not fully understood. The widely accepted mechanisms have been discussed in detail by Wu (2005). Char oxidation reactions comprise diffusion of gas species, such as O₂, H₂O, H₂, and CO, on to the surface of char pores, reactions between carbon and those gas species, and the diffusion of oxidation products out of the char pores (Tomeczek, 1994; Williams and others, 2000; Sami and others, 2001). The carbon-gases oxidation reactions involve free active sites (C_f) on the carbon surface being converted to unreactive sites (C_i) by reacting gases and the release of oxidation products from C_i to generate new C_f. C_f react predominantly with oxygen atoms over the temperature range under PC-firing conditions. The immediate product is CO that will be converted ultimately to CO₂. However, as oxygen depletes quickly and fresh oxygen diffusion through the boundary layer onto the char surface becomes increasingly difficult, reactions between C_f and CO₂ may also become important. The ratio of CO/CO₂ at the surface was found to increase with the temperature and decrease with pressure (Tomeczek, 1994).

Alongside the combustion of the organic substance in the coal, inorganic materials, either organically-bound or not, liberate from the coal and subsequently undergo various physical changes and chemical reactions to form ash. The complex mechanisms involved in ash formation have been reviewed in two earlier IEA Clean Coal Centre reports (Couch, 1994; Wu, 2005). Ash forming processes are important to the safe and efficient boiler operation in terms of slagging and fouling in the radiant and convective sections of the boiler. More detailed discussion can be found in an earlier IEA Clean Coal Report (Couch, 2006).

Coal combustion generates various gaseous pollutants including nitrogen oxides (NO_x), sulphur oxides (SO_x), and carbon monoxide (CO). Pollutants formation from coal combustion has been reviewed by Wu (2005). NO_x formation has impacts on the coal burnout. NO_x from pulverised coal combustion comprises mainly nitric oxide (NO), and much lower concentrations of NO₂ and N₂O. NO can be formed by reactions between molecular nitrogen and oxygen at high temperatures (thermal NO), oxidation of intermediate products from reactions of various hydrocarbon radicals with molecular nitrogen (prompt NO), and oxidation of organically bound nitrogen in coal (fuel NO). Fuel NO formation accounts for 70–80% of the total NO_x formed, whereas thermal NO typically contributes 5–25% and prompt NO just about 5% (Wu, 2005). NO formation mechanisms indicate the importance of reduction in both temperature and oxygen concentration in lowering NO_x emissions from coal-fired furnaces. However, this would impair coal burnout as explained in Section 2.2.3.

2.2 Factors affecting coal burnout

2.2.1 Coal properties

Coal properties strongly correlate with combustion behaviour. The first property is the moisture content of a coal, which presents a burden to coal ignition. Moisture exists in coal as either surface moisture or inherent moisture. The moisture must be vaporised and superheated during the early stage of the coal combustion process. More energy is absorbed at elevated temperatures as the water molecules dissociate. Moisture content generally increases as coal rank decreases (Kitto and Stultz, 2005). High volatile bituminous coals typically have 15% moisture content; subbituminous coals may have a moisture of about 30%. Some lignites may contain moisture in excess of 40%, which exceeds the ignition capability of conventional PC-fired systems. Alternative systems are required to boost drying during coal preparation and/or to divert a portion of the evaporated moisture away from the burners. Char burnout is impaired by moisture which depresses the flame temperature.

Drying and heating may result in significant physical changes to coal particles (Wu, 2005). Particle shrinking very often occurs due to evaporation of moisture. The extent of shrinking depends mainly on the moisture content and the coal type. The pore sizes of coal particles also reduce as particles shrink. Moreover, evaporation of moisture produces steam that has to migrate through the pores to escape the particles. If the pores are not large enough to permit rapid steam transportation, pressure will build up within coal particles and possibly cause internal cracking and fragmentation. The degree of fragmentation appears to increase with the particle heating rate. These changes to the porosity of coal particles affect their subsequent burnout performance.

Coal rank also affects the properties of volatile matter and its release. As a general trend, the volatile yield decreases with increasing coal rank. The reason seems to be the abundant chemical structures, such as $-OH$, $-COOH$, and $-OCH_3$, present in the lower rank coals. These chemical structures are easy to break up during pyrolysis. However, there is no clear correlation between the tar yield and coal rank. Generally, bituminous coals yield relatively larger amounts of tar than other coals; lower rank coals release less tars but larger amounts of light gases including CH_4 , C_2H_4 , C_2H_6 , CO , CO_2 , H_2 and H_2O (Glarborg and others, 2003). The actual composition of volatile matter depends on both coal rank and heating conditions such as heating rate, pressure, residence time during pyrolysis and the peak pyrolysis temperatures.

The morphological properties of char are also dependent on the types of parent coal. Many coals particularly bituminous coals, become softened upon heating and subsequently undergo a plastic stage (Wu, 2005). The transport of released volatiles through the particle to the surface produces bubbles in the coal mass, and the coal particle can swell by 10–15%. The bubbling/swelling phenomena generally becomes more intensive with higher heating rates. The bubbling/swelling significantly influences the particle size, porosity, and density

of the char, which all ultimately affect the char burnout. For example, Gale and others (1995) found that only pores with nominal diameters of 2–50 nm actually provide an effective surface area for the oxidation reactions of char.

The intrinsic reactivity of char also varies with coal types. Russell and others (2000) reported that chars from lower rank coals are more reactive when prepared at lower temperatures. But at high temperatures, the opposite was true because the lower rank coals are more susceptible to thermal deactivation. Zhang and Bi (2003) also found that char reactivity generally increases with the volatile matter content of coal, but that it is also subject to the actual devolatilisation conditions. The maceral composition of the parent coal also affects the reactivity of the char. A considerable difference in swelling behaviour between different maceral groups has been observed for a bituminous coal (Yu and others, 2003). The swelling became more intensive following the order inertinite < vitrinite < liptinite. However, as the coal rank increased, this difference diminished as a result of the more uniform chemical composition of maceral groups (Yu and others, 2003). All maceral groups present in a parent coal may exist in the resulting char (Carpenter, 1995). Inertinite is generally less reactive than vitrinite, while liptinite is the most reactive maceral group (Van Krevelen, 1993). The difference in reactivity between maceral groups is however significant only at lower temperatures, and diminishes above 1300°C (Stainlay, 2004). Coal minerals are known to have catalytic effects on the reactivity of char. Silica and alumina can slow down the reaction rate, whereas calcium, magnesium, iron and alkali species are able to enhance char oxidation through modification of the microstructure of char (Méndez, 2003). These catalytic effects are more pronounced for low rank coals, and become far less noticeable at high temperature (Smoot and Smith, 1985). On the other hand, mineral matter forms a barrier through which the oxygen must pass to reach the carbon. Excessive mineral content would therefore retard the char oxidation, particularly towards the end of burnout. Char fragmentation is also undoubtedly related to the nature of minerals in the char.

2.2.2 Coal particle fineness

A smaller coal particle size means lower heat transfer resistance and consequently it heats up more rapidly. This generally results in a higher volatile yield and a smaller amount of char after devolatilisation. Rapid heat transfer and combustion of smaller particles leads to higher particle temperatures. Since char oxidation reaction rates increase exponentially with temperature, char particles derived from smaller coal particles tend to burn quickly. Small char particles also benefit from high surface to mass ratios. The reduced particle size makes the penetration path of oxygen shorter, thus promoting char oxidation reactions.

2.2.3 Coal combustion conditions

Coal devolatilisation

The effect of pyrolysis conditions on coal devolatilisation is discussed briefly in this section. It is no surprise that higher

furnace temperatures favour devolatilisation of coals. Higher furnace temperatures result in a steeper temperature gradient across the radius of the coal particle. The reaction front therefore moves more quickly towards the unreacted zone within the particle. The temperatures of the reactive zone are also increased, promoting decomposition of organic coal substance. The residence time (soak time) of coal particles in a high temperature zone is also an important factor. A longer soak time means that the volatiles have more time to diffuse to the particle exterior. However, tars thermally crack at high temperatures, thus making the volatile yield gradually level off as the soak time increases. The effect of the heating rate is actually the coupled effect of the final temperature and the soak time. Hence it varies with the pyrolysis conditions as well as coal rank. Generally, at atmospheric pressure, a higher heating rate results in a higher volatile yield. At elevated pressures, the effect of heating rate becomes less certain.

Pyrolysis conditions also affect the morphological structure of the resulting char. Gale and others (2005) found that the surface area of larger pores (>2 nm) increases with temperature up to 600–700°C, but declines thereafter. Similarly, Lu and others (2001) observed an initial increase in char surface area as a result of pore growth, which, however, decreases due to coalescence of pores at the late stage of pyrolysis. High heating rates generally result in a larger proportion of cenospheres with large interior voids and thin walls. These highly porous char particles tend to break up more easily than those with thicker walls and lower porosity. Fragmentation consequently would increase, which spawns many smaller char particles, and hence the overall conversion of chars increases (Wu, 2005). The porosity of char, particularly fine pores less than 2 nm, is heavily dependent on pyrolysis pressure; more fine pores are generated under high pressure (Roberts and others, 2003). Nevertheless, the intrinsic reaction rate, that is the reaction rate normalised to the char surface area, is less affected because it is the surface area of pores larger than 2 nm that primarily take part in char oxidation reactions (Roberts and others, 2003).

Char oxidation reactions

Since volatile matter burns out within a few milliseconds, the effects of combustion conditions can be neglected. The following discussion focuses on the effects of combustion conditions on char oxidation reactions.

Temperature determines whether char oxidation is governed by the diffusion of oxidants or carbon-gases chemical reactions or a combination of the two. Figure 1 illustrates the relationship between the combustion rate constant and temperature. At temperatures lower than 700°C, oxygen diffuses easily onto the char surface so chemical reactions govern the overall oxidation rate. Oxygen diffusion becomes difficult above 1100°C where chemical reactions take place quickly. Diffusion therefore governs the overall oxidation rates. At intermediate temperatures (700–1100°C), both factors count.

Free active sites on the carbon surface C_f can be annealed to be unreactive at high temperatures, given a sufficient exposure time. Under the harsh conditions in PCC boilers, such annealing-induced deactivation may occur either at peak

flame temperature, or more gradually over the course of combustion. The deactivation can be linked to the increased degree of crystallinity of char (Hurt and others, 1995; Dong and others, 2009).

Thermal annealing has a number of important implications for char combustion. Firstly, it is intrinsically difficult to achieve high carbon burnout in a full-scale furnace as predicted by models based on laboratory char oxidation kinetics. Secondly, to identify difficult-to-burn coals during coal purchasing, it is necessary to consider not only their early combustion reactivity (normally estimated in laboratory test) but also their propensity to deactivate due to annealing at higher temperatures. The high-temperature reactivity of chars (for example carbonised at 1800–2200°C for 100–1000 ms) is more difficult to measure in a laboratory, so is not included in the ‘standard’ property profiles of power plant coals. Finally, an appropriate flame temperature and a stable flame structure are of great importance in achieving a high burnout. Since oxygen diffusion through the boundary layer governs the overall char oxidation at high temperatures, further increase in flame temperature can just accelerate the combustion slightly, but significantly anneal the char. It becomes more difficult to burn the deactivated char once it escapes into lower temperature regions. Thermal annealing is particularly detrimental to low NO_x systems, where the opportunity to consume the young and reactive char rapidly may be lost due to the deficient supply of oxygen.

Studies have shown that increasing pressure at constant gas

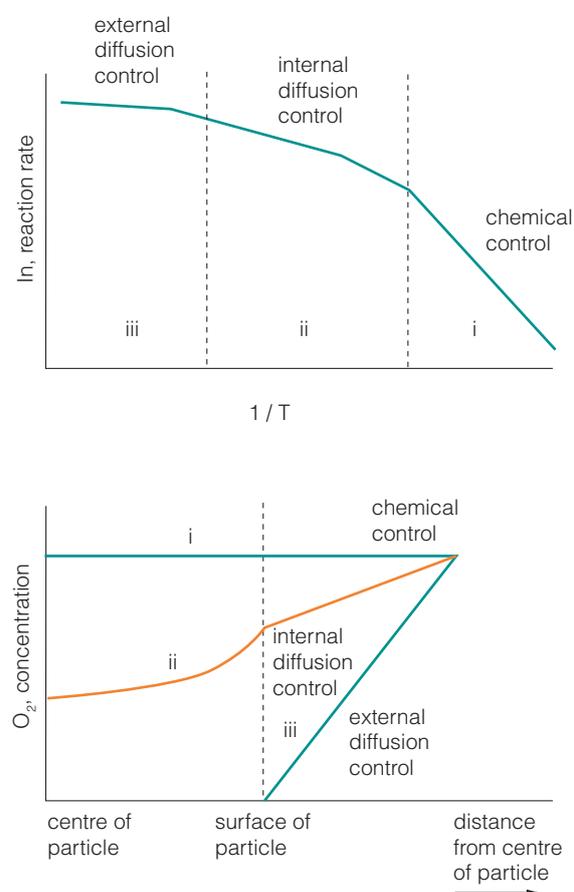


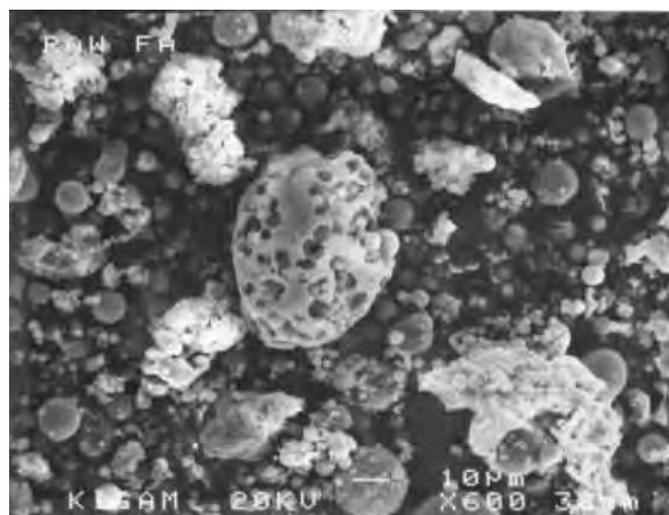
Figure 1 Reaction zones of char combustion (Williams and others, 2000)

composition increases the coal combustion rate, most strongly for low-reactivity coals that are difficult to burn completely in atmospheric pressure boilers. Saastamoinen and others (1996) discovered that the combustion rate increased significantly as the pressure increased from 0.1 to 0.3 MPa. The reason was that higher pressures thermodynamically favoured the oxidation reactions of char. In addition, the heat released from the oxidation was better retained in the particles, which resulted in higher particle temperature. Consequently, the extent of devolatilisation could increase and coal burned more quickly. However, the effect of pressure increase diminishes above 0.3 MPa (Saastamoinen and others, 1996). The effect of pressure is more pronounced at low oxygen concentration. For large particles or reactive coals, the effect is found to be small. For unreactive coals and small particles, the effect could be seen at pressures greater than 1 MPa (Saastamoinen and others, 1996).

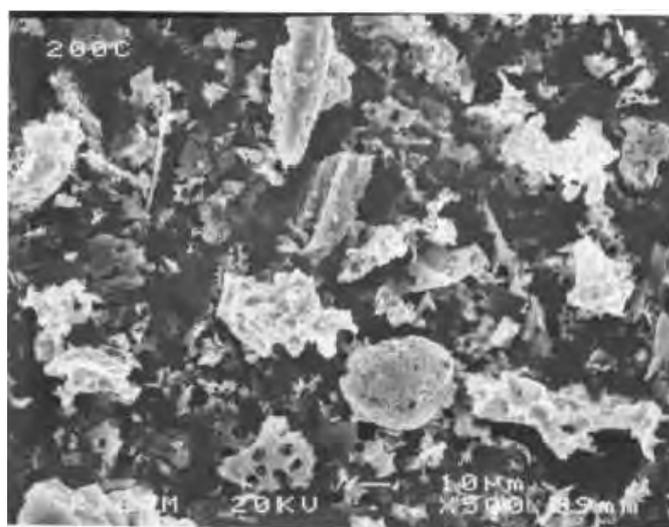
Increasing the concentration (or partial pressure) of oxygen also increases the char combustion rate due primarily to reduced delay in ignition (Saito and others, 1991). An increase of 4–10% in char burnout has been observed with a 21–75% increase in the oxygen partial pressure during 20 ms combustion runs in a wire mesh reactor (Pipatmanomai, 2002). Oxygen partial pressure was also considered as the key factor, apart from temperature, affecting the reaction order and transition from chemical kinetic control regime to diffusion control regime (Hu and others, 2001). Pore size and shape in char may also change with the oxygen partial pressure during combustion (Banin and others, 1997).

2.3 Unburnt carbon in fly ash

A knowledge of the association of unburnt carbon with the inorganic ash will help understanding of the performance of various carbon reduction techniques, as discussed in Chapter 5. An investigation has been made in this regard in South Korea (Ahn and others, 1999). Fly ash samples, with an average loss on ignition (LOI) of 8 wt%, were obtained from the Boryung coal-fired power plant in South Korea. The unburnt carbon was recovered from the fly ash using a flotation technique. The size of recovered carbon particles ranged from submicrometer to over 600 μm , with 80% in the range of 12–240 μm . The carbon content was found to increase with particle size. Microscopic examination using Scanning Electron Microscopy (SEM) revealed that the inorganic ash consisted predominantly of glassy spheres (*see* Figure 2a). Most of the unburnt carbon present was in the form of distinct, fused particles with an extensive macroporous structure. The unburnt carbon portion appeared in either nearly spherical, rectangular, lamellar, granular, vesicular or other fragmental shapes; the lamellar-shaped carbon was most easily recognised (*see* Figure 3). In none of the images examined did a significant fraction of the carbon appear to be encapsulated by inorganic matter. Many fully or slightly fused ash particles were seen on unburnt carbon particles as either spheres of various size or in the bar-like shapes (*see* Figure 4). The Energy Dispersive X-ray Spectroscopy (EDS) analyses showed that the bar-shaped ash particles consisted of only aluminium and silicon, but the smaller spherical ones contained iron, calcium and potassium



a) fly ash



b) unrecovered unburnt carbon concentrate

Figure 2 SEM image of (a) fly ash and (b) the recovered unburnt carbon concentrate (Ahn and others, 1999)

in addition. This distinct chemical difference was due to the much higher melting points of some aluminosilicate crystalline compounds which were either not or just slightly molten in the combustion zone. In contrast, iron or alkali compounds with lower melting points were more likely to vaporise and subsequently condense to form spherical particles in colder regions of the boiler.

2.4 Summary

This chapter reviews pulverised coal combustion and factors affecting coal burnout. Devolatilisation is the key step in pulverised coal combustion, affecting the stability of the coal flame and determining both the quantity and reactivity of the resulting char. Char combustion involves complex heterogeneous reactions which are considered to take place on free active sites on the char surface. Ash formation is important to safe and efficient boiler operation in terms of fouling and slagging on the steam tubes and convective heat-

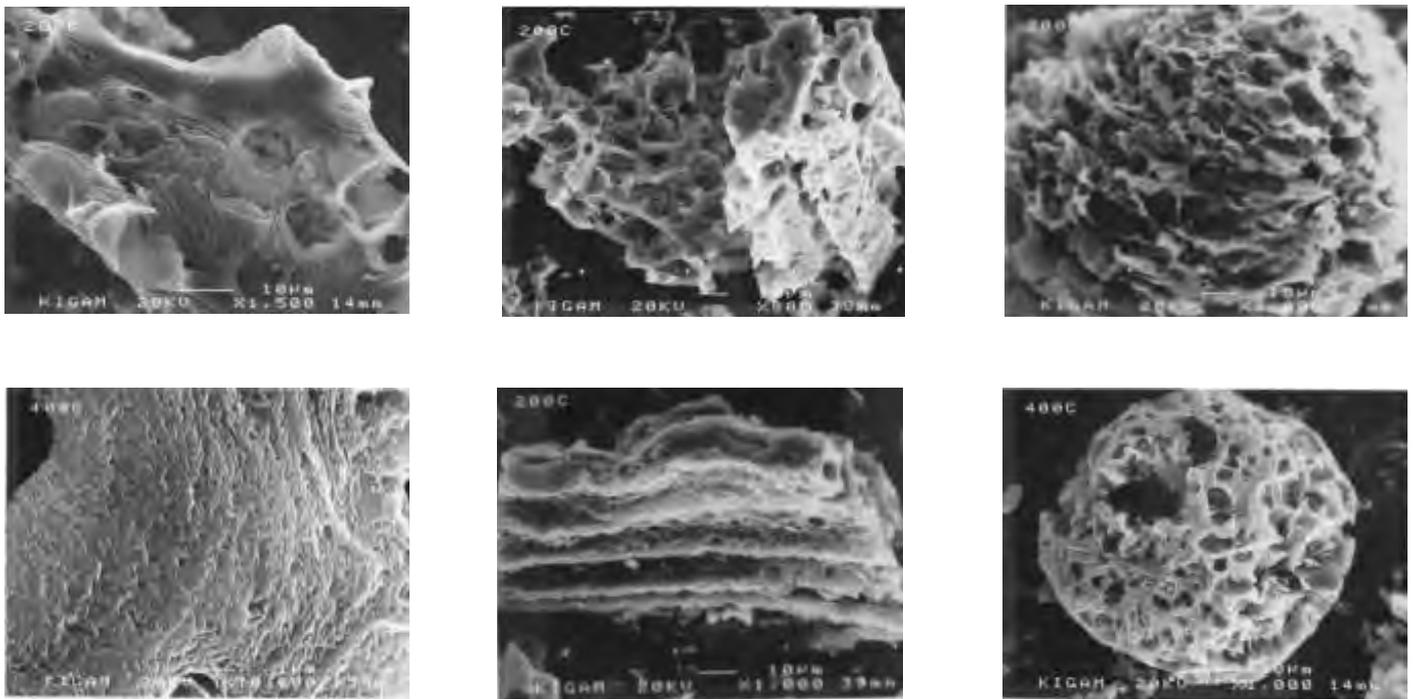


Figure 3 Various typical shapes of unburnt carbon present in the ash (Ahn and others, 1999)

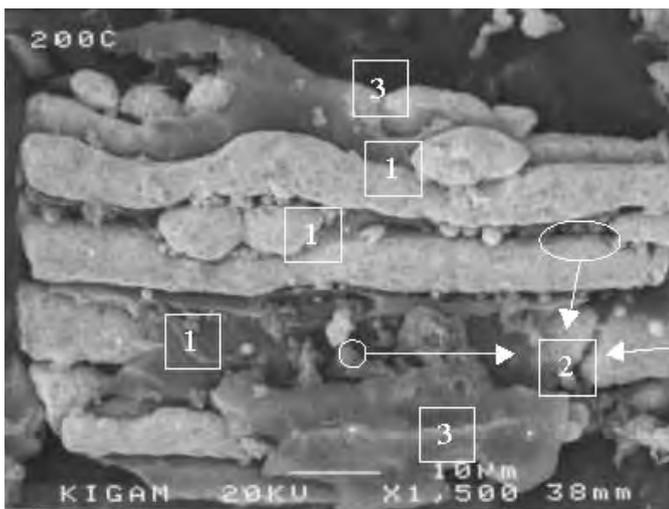


Figure 4 SEM image of the ash particles associated with unburnt carbon (Ahn and others, 1999)

transfer surfaces. NO_x is one of the main gaseous pollutants from coal-fired boilers and its reduction often leads to low burnout of coal. NO is the predominant species and is primarily formed from oxidation of organically bound nitrogen in coal (Fuel-NO).

There are many factors affecting coal burnout. Coal properties such as moisture content, volatile content and maceral composition strongly correlate with its combustion behaviour through affecting volatile yield and char intrinsic reactivity and modification to the char porous structure. Coal fineness affects the heating rates of coal particles and transportation of both oxygen and oxidation products within the particles. Coal burnout in full-scale furnaces also depends on the actual combustion conditions. High temperatures generally favour coal burnout; however, a prolonged exposure to high temperatures may anneal the free active sites on char surface and reduce the reactivity of the char. Increasing the oxygen concentration (excess air ratio) increases the char combustion rate due to reduced delay in ignition.

Microscopic examinations reveal that unburnt carbon concentrates on large particles and appears in various shapes and forms. Unburnt carbon particles are unlikely to be encapsulated by inorganic matter. Separation of unburnt carbon from ash particles is therefore feasible.

3 Preventing excessive carbon-in-ash

Measures available to improve coal burnout are based on consideration of the factors affecting pulverised coal combustion described in Chapter 2. These measures include coal cleaning, improving coal fineness, coal selection and blending, coal combustion optimisation, computer-based combustion optimisation tools, and on-line carbon monitoring.

3.1 Coal cleaning

Coal is a heterogeneous material which contains a variety of impurities. Troublesome impurities, principally ash-forming minerals and sulphur, may affect coal combustion performance in boilers and cause operating problems. Too high an ash content can dilute the heating value of coal. Consequently, more coal needs to be burned to meet the required heat output. Since ash absorbs heat and interferes with radiative heat transfer to coal particles, excessive ash particles present in the furnace inhibit the coal combustion process. In addition, ash-related slagging and fouling problems are the root of many plant outages, which in some cases affect the burner arrangement, and thus impact the coal combustion in the furnace. Coal cleaning is therefore an essential method to eliminate these potential problems.

Coal cleaning is based primarily on physical separation processes which exploit the difference in density between mineral matter and organic coal substance and their wetting properties. The effectiveness of cleaning depends on the nature of the coal. Impurities organically bound in the coal matrix cannot be removed. Chemical and biological methods may also be used, but these have not yet been applied on a commercial scale. A detailed introduction to advanced coal cleaning technology is given in a previous IEA Clean Coal Centre report (Couch, 1991).

Coal has long been regarded as a low cost fuel, so it was often difficult to justify the capital and operating costs against the benefits associated with coal cleaning. In recent years, this situation has changed as a result of considerable increases in coal and electricity prices in conjunction with more strict emission regulations. Substantial efforts in the development of coal cleaning technologies have been made in Australia, Canada, China, India, Poland, South Africa, USA and former USSR countries over the past decades. However, in coal-exporting countries such as Australia and South Africa, coals used in domestic power plants still have high ash contents of typically 30–35% (Couch, 2006). Coal cleaning is still sparse in most developing countries. As older, less efficient boilers are gradually replaced with more efficient supercritical/ultra-supercritical ones, particularly in China and India, there will be an increased demand for high-grade coals with more consistent properties. Virtually all thermal coals traded on the international market are washed, due to their higher prices.

3.2 Improvement in coal fineness

It is known that a finer particle size can effectively improve the burnout of a coal (*see* Section 2.2.2). Improvement to the fineness of coal pulveriser output is therefore an important way to minimise carbon-in-ash in PCC boilers. At least 75–80% of opportunities to improve the combustion performance of most PC-fired systems are dependent upon a reduction in coal particle size (Storm, 2006).

As an important prerequisite to coal pulverising, the raw coal fed into coal mills should be consistently less than 19 mm (0.75 in). This is typically accomplished either during coal preparation/cleaning or at the power plant using a coal crusher. Tramp mineral rocks can be effectively liberated from the organic substance during crushing. This will enhance the effectiveness of the magnetic separation process and contribute to a smooth feed of coal into the mills. A lower quantity of hard mineral rocks also reduces the erosion/wear of grinding mechanisms and outage of the mills due to maintenance. Coal is dried by hot air from air heaters to help yield a higher mill capacity; mill outlet temperature is typically in the range 54–93°C (Landers and others, 2004). The hot air, often called primary air, also transports the ground coal to the burners.

Various coals have different comminution performances. Coal properties relating to comminution are their abrasiveness and grindability. The abrasiveness of a coal is a measure of the potential wear on mill components during operation, generally indicated by its abrasion index (AI). AI is expressed in standard tests as milligrammes of metal lost per kilogramme of coal used. Grindability is a measure of the relative effect of a coal on the maximum grinding capacity of a mill when producing a product of specified fineness. The Hardgrove Grindability Index (HGI) is the standard indicator of the grindability of a coal, which derives from empirical testing. A lower HGI means a coal is more difficult to grind; consequently the mill capacity is low when the coal is ground. HGI is non-linear – for example, a change in grinding difficulty from 40 to 50 is greater than a change from 80 to 90. As an empirical parameter, HGI determination suffers poor repeatability and reliability for some coals, which may give misleading information to understand or explain the results from other coal analyses. Many efforts have therefore been made to develop new grindability indicators that correlate only to simple coal compositions. It is beyond the scope of this report to detail these developments. Interested readers can refer to Senguta (2002).

Mill output fineness is controlled using a particle classifying device to separate coarse from fine particles and recycle the coarse particles back to the mill for regrinding. Traditionally, static classifiers have been used on coal mills that offer only limited scope for coal fineness control. A dynamic type of classifier is a better solution, with the potential to eliminate almost all the coarse fraction (>300 µm) from the mill output

Case study

E.ON UK identified that retrofitting two-stage low NO_x combustion systems to units at its flagship coal generation plant at Ratcliffe-on-Soar would be required to satisfy the new NO_x emissions regulation in the Large Combustion Plant Directive (500 mg/m³ at 6% O₂). The Ratcliffe power plant had been selling a significant percentage of its fly ash (approximately 7% unburnt carbon) to cement producers (Landers and others, 2004). It was important for the plant to continue to do so after the retrofitting. It was identified that mill out fineness had to be reduced to mitigate the effects of the low NO_x systems on the ash quality. LSXS ZD dynamic classifiers were ordered from Loecsche and retrofitted to seven ball mills. Pre-retrofit data showed that 75% of the mill output could pass through a 74 µm sieve and 97.5% of particles through a 300 µm sieve with static classification. After the retrofit, a similar percentage passed through the 74 µm sieve, but virtually all particles passing through the 300 µm sieve was achieved with very few particles between 200 and 300 µm (Power, 2007). A 62% average reduction in carbon-in-ash at normal excess air ratio was observed during post-retrofit testing (Power, 2007). Moreover, the LOI of ash was found to decrease with mill output fineness. An additional payoff of the retrofit was a 13% average reduction in the NO_x emissions from the plant (Power, 2007). All reported results were from tests conducted before installing an overfire air system, thus accounting for the sole contribution from improvement in coal fineness.

(Landers and others, 2004). A typical design of dynamic classifier consists of static guide flaps and a rotor with blades. A field of centrifugal forces is formed in the gap between the guide flaps and rotor blades, which flings coarse particles back into the mills. Because the guide flaps are not adjustable, the fineness of the finished coal depends only on the rotational speed of the rotor; a higher rotor speed leads to increased fineness. Dynamic classifiers can also increase the throughput of a pulveriser while maintaining or even improving the output fineness. Experience with vertical-shaft pulverisers suggests that replacing a unit's static classifier with a dynamic classifier will increase its throughput by more than 30% and simultaneously increase coal fineness by 10% (Power, 2007). Adoption of dynamic classifiers may also result in a lower oxygen level in the furnace, an additional benefit to NO_x reduction (Landers and others, 2004). Moreover, other issues related to poor coal fineness, such as slagging propensity and SCR catalyst wear, may also be alleviated. In spite of the paramount importance of mill output fineness to carbon burnout and NO_x reduction, capital investment into coal pulverising systems is often low.

3.3 Coal selection and blending

Competition from natural gas fired combined cycle gas turbine and tightening emissions regulations have imposed increasing pressures on power plants operators to diversify their fuel sources. For example, a number of US power plants

have switched their fuels to the low sulphur subbituminous coals from the Powder River Basin (PRB) of Wyoming in recent years and the trend is still increasing. In the UK, after the closure of many coal mines, utilities are relying on imported coals and seeking cheap coals to reduce their generation costs. Using unfamiliar coals may yield problems for the power plants. For example, some imported low-volatile coals may be difficult to burn due to poor ignition and flame stability, thus resulting in increased carbon-in-ash. Low sulphur PRB coals may lead to degraded performance of electrostatic precipitators (ESP). Some coals may have a higher potential for NO_x formation. A common solution to most of the fuel-related problems is to blend coals to produce a mix with properties in the range that a power plant can accommodate. Given the limited blending capabilities in most plants, simple binary blends are common in practice. In OECD countries, coal blending may be the preferred way to improve the performance of existing power plants where system modifications can be costly and sometimes constrained by the fixed designs of boilers and auxiliary equipments. Coal blending for power stations has been reviewed in detail in a previous IEA Clean Coal Centre report (Carpenter, 1995).

The growth in the international thermal coal market has provided many electric utilities with a wider selection of coals. Global trade in hard coal in 2006 rose by nearly 35% from the 2000 level, amounting to 613 Mtce (million tonnes of coal equivalent) or 14% of total hard coal output. Feedstock from Australia, Canada, China, Colombia, Indonesia, Poland, South Africa, the USA, countries of the former USSR and others are now available. The properties of coals from the various geographical regions differ in their ash chemistry and petrographic composition. The criteria for selection of acceptable coals for blending is based on minimisation of adverse impact on the power plant performance. Prediction of blend combustion behaviour is therefore important for making blending criteria and intelligent coal selection prior to fuel procurement.

There are generally two approaches for prediction of the combustion behaviour of blends: empirical predictive indices and bench/pilot-scale testing. The principle for empirical predictive indices is that the properties of a blend can be calculated as the weighted average of the properties of component coals in the blend. Commonly used are the fuel ratio (fixed carbon/volatile matter), Dulong's heating value, B&W's ignition factor (volatile matter × coal oxygen), and many indices based on coal petrographical characteristics. These indices are useful to indicate the ignition, flame stabilities and carbon burnout. Coal properties data used in these indices are determined using national or international standard tests, including heating value, proximate and ultimate analyses, petrographic analyses, free swelling index, ash fusion temperature and grindability (HGI). Of these properties, moisture, volatile matter, ash, fixed carbon, C, H, S, N, O, Cl and maceral contents and heating value appear to be additive; however, care should be taken in the application of the additive rule for the volatile matter and ash content (Carpenter, 1995). The free swelling index, ash fusion temperatures and HGI are generally non-additive (Carpenter, 1995). It is the 'non-additivity' of some of the coal properties

that make the predictions inherently complex, even for a simple binary blend. For example, some binary blends (1:1 by weight) may have higher combustion losses, that is the percentage of carbon remaining unburnt, than either of the component coals (Irons and others, 1999).

Since coal is a complex heterogeneous material, coal particles of different organic or inorganic composition can behave in completely different manners. It is not surprising that some coals that appear to be acceptable on the basis of proximate and ultimate analyses may have unexpected burnout performance. The reason is partly the difference in their petrographic composition, which lies not only in the presence or absence of particular maceral groups, but also in the way in which these macerals are associated together (microlithotypes). In general, exinite, most of vitrinite and low reflectance semifusinite (an inertinite group maceral) are reactive, whereas oxidised vitrinite, high-reflectance vitrinite and the rest of the inertinite group are unreactive (Cloke and Lester, 1994). Maceral reactivity depends not only on its type but also on the rank of the original coal (Barranco and others, 2003). It is the unreactive macerals that contribute primarily to carbon-in-ash. However, so far there are no standard methods to define the reactivities of various maceral groups under PC-firing conditions. Furthermore, the behaviour of macerals within coal particles may differ from that in their isolated state; forms and distribution of microlithotypes thus greatly affect the reactivity of a coal. The microlithotype analysis is suggested to be more valuable than simple maceral analysis in prediction of coal combustion behaviour (Cloke and Lester, 1994). The mineral matter also influences the char reactivity, with certain cations having catalytic effects (Serio and others, 1987). Char porosity is another main factor affecting char reactivity, which is highly dependent on both the coal swelling property and the combustion conditions. All

the above factors determine that any predictions based on one or two coal properties alone may be misleading and their usefulness limited.

To improve the reliability of empirical predictive indices, some efforts have been made to develop indices involving a number of properties of component coals. The Coal Stability Index (CSI), for example, combines the higher heating value of the volatile matter with petrographic reflectance analyses to evaluate the ignition and flame stability of blends (*see* Figure 5). CSI is defined as follows:

$$\text{CSI} = \frac{\text{HHV}_{\text{vol}}}{\text{BRI}} \quad 1$$

where, HHV_{vol} is the higher heating value of volatile matter (% , ASTM D3175) on a unit mass of coal basis; the Bimaceral Reflectance Index (BRI) is determined from the petrographic reflectance analysis of the coal. It was found that coals with $\text{CSI} < 25$ showed unstable flame characteristics. Thus CSI can be used to determine the maximum proportion of low-volatile coals with unstable flame characteristics in a blend (Breen and others, 1991). However, its applicability to blends of inertinite-rich coals or coals with distinct petrographical properties requires further investigation. Su and others (2001) proposed a compounded maceral index that indicates the reactivity of a coal. The index involves the maceral composition, mean vitrinite reflectance and heating value of a coal, and is defined as follows:

$$\text{MI} = \text{RF} \times (\text{HVF})^{2.5} \quad 2$$

$$\text{HVF} = \frac{\text{HV}}{30} \quad 3$$

$$\text{RF} = \frac{L + \frac{V}{R^2}}{1^{1.25}} \quad 4$$

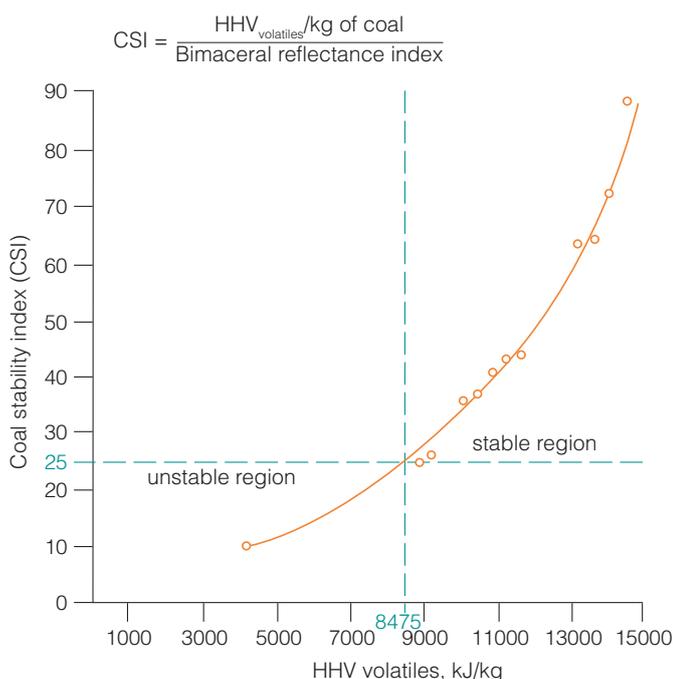


Figure 5 Correlation between CSI and HHV of the volatile matter (Breen and others, 1991)

Where HV is the heating value of a coal or blend in MJ/kg. HVF is a factor normalised to a typical coal heating value (30 MJ/kg, air dried), and represents the influence of moisture and ash content of a coal on its ignition and flame stability. L is the liptinite percentage by volume on a mineral matter free basis; similarly, V is the vitrinite percentage and I is the inertinite percentage. R is the mean maximum vitrinite reflectance. In general, a higher MI value indicates the fuel is more reactive and easier to burnout.

Most maceral predictive indices do not differentiate reactivities between different sub-maceral types of a given maceral. For example, a considerable proportion of inertinite, the semifusinite, may be similar in reactivity to vitrinite. Helle and others (2003) took this into account and modified Su's reactivity index. The modified version, reactive maceral index (RMI), was found to be useful to estimate the deviation of actual burnout from values calculated from the weight average of burnout of component coals (Helle and others, 2003). If component coals of a binary blend have similar RMI values, the deviation is generally small; a large deviation has been found for blends made up of coals having distinct RMI values.

So far, no empirical predictive indices have robust reliability

in predicting combustion behaviour of blends. The complex nature of coal appears to be the underlying reason. In addition, questions arise as to whether the milligrammes or grammes of samples used in the standard analyses for determining coal properties can provide truly representative samples of the tonnes of coal consumed in a boiler. It is important to follow standard procedures for collecting samples as specified in various national and international standards in order to minimise any bias. Moreover, most standard tests do not reflect the actual combustion conditions in power plant boilers. Empirical predictive indices based on standard analyses may therefore lead to inaccurate predictions. Testing is highly desirable, which can closely represent conditions in full-scale PCC boilers.

Such tests can be conducted in either bench- or pilot-scale rigs. In addition to providing close-to-full-scale conditions, these tests are also much cheaper and more flexible than trials on full-scale boilers. Some widely-used bench-scale rigs include the thermogravimetric analyser (Carpenter and Skorupska, 1993; Carpenter, 1995), the wire-mesh apparatus (Anthony and others, 1974; Suuber and others, 1980; Gibbins, 1988; Kandiyoti and others, 2006) and the drop tube furnace (Serio and others, 1987; Carpenter and Skorupska, 1993; Card and Jones, 1995; Kido and Hirasawa, 1988; Barranco and others, 2003).

Pilot-scale testing systems can resemble the combustion conditions in full-scale boilers most closely. Ignition and flame stability, carbon burnout and NO_x formation of pulverised coal combustion have been investigated in pilot-scale testing systems. Design and configuration of pilot-scale testing systems vary considerably, depending on the specific research purposes. Two combustion test facilities (CTFs), owned by UK utility companies, are introduced briefly as follows to illustrate the role of pilot-scale testing systems in investigating coal burnout performance, (Elston, 2003).

Npower's 1 MWth CTF was designed as a convenient tool to provide realistic, closely controlled combustion conditions for studying burnout of pulverised coals. The CTF was designed on the basis of residence time scaling so that it provides an accurate simulation of the time/temperature profile of the full-scale plant. The facility is fired by a single horizontal low NO_x pulverised-fuel burner with a tertiary/secondary air ratio of 3.5:1. Overfire air (OFA) can be injected through ports located in the convective section for air staging tests. Flue gas composition is monitored continuously. Partially burned char samples can be taken from different ports using a quench probe for further analysis. A correlation between fuel ratio and combustible loss, based on results from CTF tests, is given in Figure 6. The fuel ratio is the ratio of fixed carbon to volatile matter derived from proximate analysis of coals tested. The combustible loss is the percentage of the original coal left unburnt. It can be seen from Figure 6 that the level of unburnt carbon is very sensitive to the excess oxygen level and that air staging tends to result in a higher level of unburnt carbon. There is also a broad trend that coals with higher fuel ratios are more difficult to burn out completely.

The CTF of E.ON UK represents a scaled model of the flue gas path in a typical 500–600 MWe UK power plant. The

scaling criterion was the same as that used for Npower's CTF, the constant residence time of coal particles. The time/temperature history of a coal particle is thus similar to that of a particle fired through a middle row burner with its residence time being approximately 2 s. The peak flame temperatures are similar to a burner surrounded by other firing burners. The CTF, rated at 0.5 MWth, is designed for fuel testing and can fire solid, liquid or gaseous fuels either alone or in combination. In coal testing, the carbon-in-ash sample is taken just after the convergent section located downstream of the combustion chamber. Results from coal testing in this CTF revealed the relationship between coal quality, grind quality and excess air with respect to the level of carbon-in-ash. A detailed discussion can be found in Elston (2003).

In addition to coals, coal blends have also been widely studied in pilot-scale combustion systems. Some important conclusions from these studies are summarised below.

- Blending with a higher volatile bituminous coal at an appropriate ratio (1:2 in the reference) can improve the ignition and flame stability of a low volatile bituminous coal (Douglas and Krcil, 1994)
- Adding a more reactive coal to a blend can, in some cases, improve the burnout performance (Lee and Whaley, 1983; Douglas and others, 1990; Irons and others, 1999). The reduced unburnt carbon content in the fly ash results both from enhanced carbon burnout of the less reactive coals in the blend and from the dilution effect of fly ash from the more reactive coals.
- Blending a less reactive coal with a more reactive coal may not necessarily enhance the burnout of the former under both air-staged and unstaged conditions (Lee and Whaley, 1983; Smart and Nakamura, 1993; Irons and others, 1999). The reasons are complex and closely linked to specific plant operating conditions and fuel properties. For example, when a low volatile, high HGI (easier to grind) coal was blended with a high volatile (more reactive), low HGI coal, the carbon burnout levels

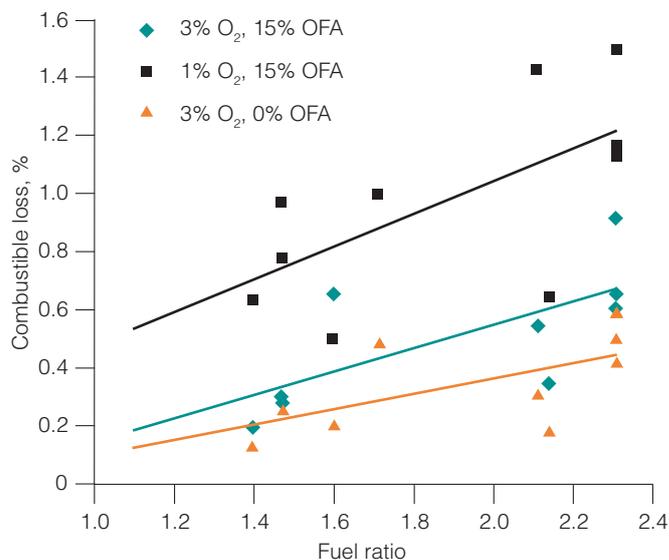


Figure 6 Npower's CTF test: fuel ratio versus combustible loss (Elston, 2003)

of the blends were found to be similar to that of the low volatile coal alone (Lee and Whaley, 1983). This was because the more reactive coal was more difficult to grind, resulting in coarser mill output; the increased coal size tends to adversely affect coal burnout. Another reason might be that faster consumption of oxygen by the more reactive coal in the initial stage of combustion deprives the less reactive coal particles of oxygen, thus inhibiting their burnout.

- Under air-staged conditions, a shorter residence time of blends in the primary zone can reduce the deviation of carbon burnout from the predicted level (Lee and Whaley, 1983; Kambara and others, 1992; Maier and others, 1994). The predicted carbon burnout of a blend is the weighted average of the carbon burnout for its component coals when the coals are fired alone.

3.4 Optimisation of coal combustion

This section discusses optimisation of coal combustion in boilers, which represents the most important step to reduce the carbon-in-ash. The principal challenge is to improve coal burnout effectively without increasing NO_x emissions. The following discussion is based on a report by Babcock & Wilcox on full-scale low NO_x PC-firing combustion systems (Kitto and Stultz, 2005), with additional information on the subject being incorporated.

3.4.1 Increasing combustion air temperatures

Higher air temperature favours the quicker ignition of coal and consequently longer residence times for combustion in the furnace. The temperature of PA/PC mixture in coal mills should be as high as possible without exceeding the explosive limit. Mill inlet temperatures may be around 149°C for low moisture coals and around 371°C for high moisture coals; mill outlet temperature ranges from 54°C for low rank coals to 93°C for high rank coals. Such low PA temperatures can not play a significant role in rapid coal ignition, while the SA temperature is important. SA temperatures, typically 316°C, are controlled by heat transfer from tubular or regenerative air heaters. Some special design of the air heater can be used to boost the secondary air temperature for some coals that are difficult to ignite, such as low volatile bituminous coals. Both the mill exit temperature and the secondary air temperature at windbox inlet should be monitored continuously. Optimum gas temperatures can be controlled by regulating the flow of 'cold' tempering air with hot air from air heaters (Soud, 1999).

3.4.2 Reducing air/fuel distribution imbalances

Fuel distribution imbalance can occur partly because of variations in raw coal feed rate to coal mills, so crushing raw coal into smaller and uniform sizes before feeding into the mills is therefore important. A lack of accurate primary air or

coal feeding measurement and control, as is commonly the case with ball tube mills, restrains the optimisation of downstream coal combustion and causes operational inconsistencies. Accurate primary air and coal flow measurements are required to minimise variations in mill output. Both air flow meters and pulverised coal flow meters are commercially available, most of which are based on either passive electrostatic detection or on microwave-based sensors. An excellent review on equipment for pulverised coal flow rate measurement, coal distribution control and coal particle size distribution measurement is given in a DTI report (2001).

Another aspect of fuel imbalance concerns non-uniformities in coal distribution among pipes from mills to the burners. The distribution of the PA/PC mixture among burner lines is dependent on the flow patterns of air and coal particles at the mill exits, as well as the flow resistance in the individual coal pipes. There are fixed geometry devices to assist in achieving even distribution of coal among burners. Riffle devices were originally installed in the coal pipes, and improved designs using plates to divide the flow into alternative directions have been developed. For example, 'egg boxes' are of a chequer board design and are aimed at breaking up coal ropes prior to entry into a riffle device. More recently, ramps have been installed in pulverised coal pipework, immediately upstream of trifurcators, to improve the coal distribution. Adjustment of the location of the ramp is key to achieving acceptable coal distribution. Ramps are expected to break up pulverised coal ropes, but may simply direct the coal flow towards the centre of the trifurcator. The performance of ramps at low mill load is less certain. Despite the use of fixed devices, uneven distribution of pf still inevitably occurs. Until a decade ago, the only method available to assess pf distribution was isokinetic sampling, which however has inherent measurement inaccuracies and is labourious and expensive. Over the past decades, pf flow measurement instruments have been actively developed. The majority of these pf flow meters are based on one of three physical principles: electrostatic detection (for example, ABB Automation PFMaster®), microwave injection and acoustic measurements (DTI, 2001). However, the accuracies of these pf flow meters (air flow meters as well) are still less satisfactory and their operation has not been reliable.

An integrated pulverised coal flow measurement and on-line control system can greatly enhance the control capability of plant operators (DTI, 2001). However, at present there are very few proven methods for on-line control of pulverised coal distribution in response to signals from a pulverised coal flow meter. Most notable are Foster Wheeler's three-way adjustable splitter and GE Energy's adjustable coal flow damper device (DTI, 2001). Foster Wheeler's adjustable splitter consists of two interleaved angle iron fingers, which can be rotated in the pipe to redirect the coal flow, and a plate that influences the air distribution. This splitter has been tested only on vertical pipes and its configuration of on-line adjustment is only valid for a particular coal or mill operating condition. Coal stratification in horizontal pipes is believed to be the reason; Foster Wheeler planned to employ a rope-breaking device upstream to extend its application. Details of those trials, however, have not been released. GE Energy's damper device takes the form of two V-shape notched plates

that form a square hole where they overlap. In this way, the device adjusts the dirty air distribution and therefore affects pulverised coal distribution among burners. The effect of the dampers is non-linear with no noticeable effect until the pipe area is reduced considerably. It controls the coal distribution at the expense of reduced primary air velocity and static pressure. The suitability of such devices depends on the margins of mill primary air fan power and the desired primary air velocities to be throttled. Reports of the effectiveness of this type of device for balancing pulverised coal distribution are mixed, and depend to a large extent on the initial causes of the imbalance.

Secondary air imbalance among burners can exacerbate the fuel imbalance problem. Many modern burners are equipped with air measurement and adjustment hardware to correct this imbalance. Furthermore, the PA/PC mixture travelling to the burners must be transported above a minimum velocity, typically 15 m/s, to prevent coal particles from dropping out of suspension in horizontal runs of coal pipes. The minimum velocity is the greater of two: the minimum primary air flow required for the pulveriser and the minimum required to satisfy coal pipe velocity limits. Distribution of secondary air among burners in a windbox can be facilitated by several means and to varying degrees of uniformity. Maldistribution of secondary air may result from variations in its pressure and velocity within the windbox, which are affected by the physical size of the windbox and the arrangement of burners. Installing adjustable dampers or registers onto the burners may provide a means to balance secondary air distribution. Modern burners are equipped with air flow measurement devices to facilitate adjustment for uniform secondary air distribution.

3.4.3 Increasing air-coal mixing rates

Air/fuel ratio and air-coal mixing rates affect coal combustion directly by influencing such factors as flame stability, flame shape and emissions. Adjustments that increase mixing rates can reduce unburnt carbon content, but increase NO_x emissions. Overall air-coal mixing rates are influenced directly by a combination of several factors. Burners initiate the mixing process of secondary air with the PA/PC mixture. Overfire air in an air-staging system supplies the remaining secondary air to the process. Flue gas recirculation to the furnace hopper or tempering ports, used for steam temperature control, adds additional flow and mixing dynamics to the furnace. Mixing inside the furnace thus results from both expansion of high-temperature combustion products and flow energies of primary air, secondary air, overfire air and flue gas recirculation. The specific size and structure of the furnace enclosure also influence the air-fuel mixing rate. The following discussion covers wall-fired systems and corner-fired systems, the two most widely-used furnace structures.

Wall-fired systems

Air-coal mixing rates vary considerably with the burner type in wall-fired systems. The simplest burners inject the fuel and air in parallel or concentric streams; entrainment of adjacent flow streams occurs as the jets develop and due to

combustion-induced expansion. Burner mixing can be induced by the PA/PC streams, the secondary air streams, or a combination of the two. For the PA/PC stream, the most frequently-used burner mixing devices are deflectors (impellers), bluff bodies and swirl generators. Deflectors are frequently installed near the exit of the burner nozzle to cause the PA/PC stream to disperse into the secondary air. These deflectors can also reduce axial momentum of the fuel jet, reducing flame length. Bluff bodies are sometimes used to accelerate the PA/PC flow locally around the upstream side of the bodies and generate recirculation on the downstream side, which promotes mixing. The bluff body can also lead to an increased residence time for a portion of the fuel near the burner, thereby increasing the flame stability. The PA/PC mixture stream may also be divided and injected as multiple streams in order to increase the surface area of the mixture streams, and hence the overall combustion efficiency.

Generating secondary air swirl is the most common way to induce air-fuel mixing for circular throat burners. Swirl generators are used upstream of the burner throat to impart rotating motion to the secondary air, which then leaves the burner throat with axial, radial and tangential velocity components. Radial and axial pressure gradients therefore form downstream of the throat, with the lowest pressure being close to the centre of the throat; the pressure gradients increase with the swirl intensity. The pressure gradients cause the secondary air stream to reverse and travel back to the lower pressure regions. Recirculating flow patterns are thus generated nearby the burners, promoting air-coal mixing in these regions. In addition, deflectors and bluff bodies are used to induce localised mixing of the secondary air stream. Low NO_x burners frequently divide the secondary air into two or more streams for which swirls may be imposed at different rates to satisfy flame stabilisation requirements while limiting the overall air mixing rate.

Burner mixing intensity is directly related to burner throat velocity, which is a key design parameter and varies considerably with the burner type. However, higher burner throat velocity increases air-fuel mixing in the furnace at the expense of burner pressure drop, which means higher power consumption by the forced draft fan. Increased air-coal mixing generally improves carbon burnout, but also increases NO_x emissions. Throat velocity decreases when the boiler firing rate (so the boiler load) decreases. Generally, optimal air-coal mixing is achieved at reduced boiler loads by operating with fewer burners in service but at higher firing rates.

Low NO_x burners have been installed on newly built PCC boilers and retrofitted to many existing PCC boilers to reduce NO_x emissions. A detailed introduction to low NO_x burners can be found in a previous IEA Clean Coal Centre report (Wu, 2002). In low NO_x burners, overall air-coal mixing is reduced to some extent and the flame envelope is larger compared to rapid mixing conventional burners. As a consequence, the quantity of unburnt carbon tends to increase. This tendency can be counteracted by careful control of burner aerodynamics and overall combustion system design. In most cases, upgraded coal preparation and improved coal fineness and size distribution are required to limit unburnt carbon to acceptable levels.

Air staging is frequently used in conjunction with low NO_x burners to reduce NO_x emissions further. Air staging involves removing a portion of the secondary air from the burners to reduce oxygen availability in the primary combustion zone and reinjecting it through NO_x ports into the furnace later in the combustion process. Often the NO_x ports are located above the primary combustion zone; therefore the term overfire air (OFA) is commonly used for such air-staging arrangements. However, the staged air may be injected below the burner zone, depending on the layout of the combustion system and furnace. Application of OFA to an existing wall-fired system reduces air-coal mixing close to burners, which can impair flame stability and slow down the combustion process. It is observed that carbon-in-ash generally increases with the proportion of the entire secondary air used as OFA; however, no simple correlations have been found between these two (Whitehouse and Riley, 2008). The major reasons are the lower SA/PC ratios and the reduced air-coal mixing. The burner throat velocities need to be increased to compensate for the reduction in air-fuel mixing. This can be achieved, in some cases, by using smaller burners with good combustion performance. Optimised burner arrangements and stronger SA swirls can also lead to better air-coal mixing in the burner zones.

Air staging may result in more chars escaping from the primary combustion zone. To ensure their complete burnout in lower temperature regions, good mixing of OFA and these char particles is of great importance. The challenge is to favour further char combustion without considerably promoting NO_x reformation. A high injection velocity of OFA through the NO_x ports is preferred in order to enhance OFA-char mixing. This translates into a design with fewer ports with high mass flow and velocity. But OFA must also be adequately dispersed across the entire furnace, which necessitates a large number of smaller ports. Furthermore, the locations of NO_x ports also require careful consideration. Ports located closer to the burners provide more time for mixing before char particles reach the furnace exit, whereas locating ports further away from the burners is more effective in NO_x emissions reduction. A combination of experience, model-assisted design and on-line tuning is therefore necessary to implement any air-staging technologies successfully.

Considering the importance of mixing of OFA with char particles, Nalco Mobotec developed the ROFA® technology (Nalco Mobotec, 2009). This technology is based on Nalco Mobotec's patented design for setting the volume of the furnace in rotation via an asymmetric boosted OFA system. The induced rotation and turbulence prevent laminar flow and result in superior mixing and temperature distribution for more effective combustion. This system has demonstrated significant NO_x reductions (typically 45–65% reduction with no chemical injection), with lower reagent use or no need for a reagent whatsoever. ROFA® also allows for the flexibility to fire various fuels and cofire biomass. Since the ROFA® system creates a secondary zone of combustion in the downstream area to the burner-combustion zone, char burnout can be increased effectively.

Corner-fired systems

Retrofitting OFA has proven to be one of the most cost

effective and reliable modifications for NO_x emission control in corner-fired boilers. Application of OFA to a corner-fired system involves diverting a portion of the auxiliary air to an overfire zone located either at the top of the windbox through two or more air compartments and/or through separate ports located some distance above the top coal elevation. Generally, separate ports are more effective for NO_x reduction, and also more flexible in their sizes and locations. Similar to wall-fired systems, corner-fired systems also require optimisation of air-coal mixing in the furnace to reduce the impact of NO_x emission control on carbon burnout. Considerations in this respect are similar to those discussed above for wall-fired systems. For example, to maintain the injection velocity of auxiliary air, the existing auxiliary air compartment and damper sizes need to be reduced, normally using blocking plates, and the auxiliary air nozzles need to be replaced with

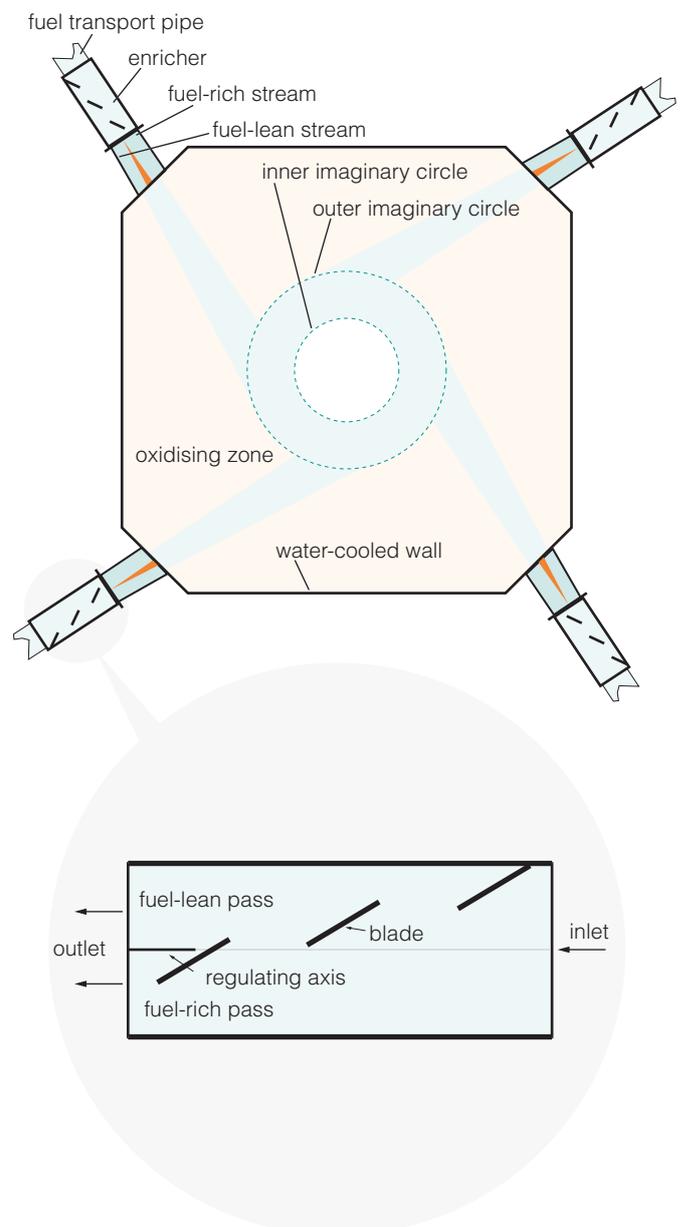


Figure 7 The schematic diagram of the fuel staging enabled by using a Louver fuel enricher on a tangentially-fired boiler (Sun and others, 2000)

smaller ones. With careful system design and on-line tuning, NO_x emissions can be controlled with reasonable unburnt carbon levels.

Fuel staging is another means to reduce NO_x formation in boilers. An example is the horizontal off-stoichiometric (bias) combustion concept developed in China in the late 1980s, as shown schematically in Figure 7 (Sun and others, 2000). A fuel enricher, called the Louver enricher as shown in Figure 7, is installed in each of the fuel transport lines, and splits the horizontal PA/PC stream into two substreams with a large difference in fuel concentration. The coal concentration of the fuel-rich substream can be several times larger than that of the fuel-lean substream. The two substreams are directed into the furnace from the same elevation with an angle (typically between 0–15°) between their axes. The fuel-rich substreams form a high temperature flame core in the central zone of the furnace, while the fuel-lean substreams form an outer layer of a more oxidising atmosphere blanketing the high temperature flame core. Fuel staging is thus arranged within the furnace. It has been reported that the horizontal bias combustion burners could reduce the unburnt carbon by 3–4.4% in an anthracite-fired boiler, corresponding to a 1–1.5% improvement to the combustion efficiency of the boiler (Sun and others, 2000). The boiler performance can be optimised further by varying the tilt angle of the regulating blades of the Louvre enrichers.

3.4.4 Adjusting excess air ratio

Monitoring of oxygen and CO concentrations in the flue gas are used to set operational levels of combustion air supply. The CO level is the most reliable guide to optimum combustion used by control systems and can be used to trim the level of excess air. However, a high CO level of flue gas might be caused by just one burner/mill group, so it is important to correctly identify the problematic burner/mill group. Although a high excess air level will result in a low CO level, it may offset the boiler efficiency due to increased dry gas heat loss (that is energy wasted by heating excess air that is not needed for complete combustion). It also increases NO_x formation, consequently placing a further constraint on the maximum excess air level permitted. Air leakage from cracks, tears and miscellaneous openings on the boiler needs to be minimised. This ingressing air provides little or no benefit to combustion because it is cold and does not mix well with the coal. However, it is measured spuriously as excess air by instruments located at the boiler outlet, which in turn reduce air feed rate to the primary combustion zone and/or the OFA zone to maintain the target excess air. Consequently, there is inadequate air in these zones to permit good coal combustion.

3.4.5 Increasing residence time of coal particles

Furnace residence time of coal particles, combined with oxygen availability, furnace combustion conditions and coal reactivity, determines the level of carbon-in-ash. Full-load residence times can vary from 1 to 3 seconds depending on burner location, furnace geometry, and operating conditions. Coal residence time is constrained by the existing boiler

design; coal burnout is expected (though dependent upon the temperature at the furnace exit) to stop when the coal particles reach the convective pass. Low NO_x combustion methods and varying boiler load may reduce burnout time by up to 50%; this is especially true given the increased installation of OFA systems (Johnson and Lockert, 2005). This residence time shortfall may be offset partially by increased air-coal mixing, but with some increase in NO_x emissions.

3.4.6 Computer-based combustion diagnostic tools

Combustion diagnostic tools can identify problem-stricken burners and furnace locations where poor combustion occurs. Most combustion diagnostic tools use either flame spectroscopic analyses or non-intrusive flame visualisation techniques to diagnose coal combustion processes (Hernández and Ballester, 2008; B&W, 2009; Dantec Dynamics, 2009).

Flame spectroscopic analyses require the collection of radiation in narrow bands associated with chemiluminescence of excited radicals, such as OH, CH and NO. The quantity and distribution of such radicals are related to coal combustion conditions. An example of such tools is Dantec Dynamics's combustion LIF systems that can be applied to pre-combustion, combustion and post combustion diagnostic applications. The LIF system uses laser-induced fluorescence and allows for species selective measurement. It is capable of measuring a wide range of combustion radicals (imaging them in two dimensions), whole-field flame front visualisation and species concentration mapping (Dantec Dynamics, 2009).

Visualisation is an invaluable diagnostic tool since it provides information on the spatial distribution of relevant variables that is helpful to describe and understand important features of a flame. Although a wide range of visualisation techniques exists, recording radiation naturally emitted from the flame appears to be the most feasible and widely-used method. It avoids the need for seeding or external illumination and is amenable to low-cost, robust CCD cameras. Quantitative information about some combustion variables can be extracted from visualised images with the aid of other measurement techniques. For example, temperature distribution across a flame can be obtained using pyrometry (Hernández and Ballester, 2008). Alternatively, certain features extracted from flame images can be interpreted as the 'fingerprint' of a particular combustion state. For example, the flame length can be used as an indicator of staged combustion. Feature extraction actually reduces the amount of information required to present a flame image. Important features extracted include geometric parameters, variables related to the level and spatial distribution of luminosity or colour, or combinations of some of these geometric parameters and variables. In addition, characteristic frequencies, derived from high-speed images, can also be used as a relevant flame feature either by themselves or combined with other image-derived properties (Hernández and Ballester, 2008). In practical applications, flame features, however, need to be related to known combustion situations or to measurable combustion parameters. For example, the

luminosity feature, derived from flame images acquired at two wavelengths, has been related to the carbon-in-ash content (Shimoda and others, 1990). Baek and others (2001) also found a linear relationship between an image-derived chromatic parameter and NO_x emissions as well as the unburnt carbon in a pilot-scale furnace. Artificial neural networks can be used as fitting tools to relate image features to relevant combustion parameters. Using flame visualisation for combustion control or optimisation has been reviewed by Hernández and Ballester (2008).

Flame Doctor™ is a commercial flame-visualisation combustion diagnostic system offered by Babcock & Wilcox (2009). Flame Doctor™ analyses signals from existing optical flame scanners to diagnose poor operation in individual burners, often the cause of excessive carbon-in-ash. It includes a portable hardware and software package designed for utility and industrial coal burners. The portable system supports the combustion tuning services offered by Babcock & Wilcox; the system is also designed for permanent installation. The main hardware components comprise a central data acquisition system for collecting flame scanner signal output and a computer-based signal processor and

display. Usually it is possible to use output from existing optical flame scanners with little or no modification. The core of the system is a set of proprietary mathematical tools to detect characteristic shifts in flame patterns from the optimal so as to diagnose combustion problems. Once the scanner signals are processed, Flame Doctor™ makes an immediate assessment for each individual burner. A flame ‘quality’ map for the furnace is then displayed on the graphical user interface. With this information, individual burners can be adjusted to optimise overall performance in spite of load changes, fuel quality variations and equipment deterioration.

3.5 Enhancement of combustion by plasma technology

Enhancement of PC combustion, particularly for high ash/moisture or low volatile coals, can ensure a satisfactory burnout performance. Conventional low rank coal enrichment processes can diminish the ash and moisture contents, but cannot increase the reactivity of a coal because the volatile content is not increased. This has stimulated the development of a modern plasma-based technology for coal combustion

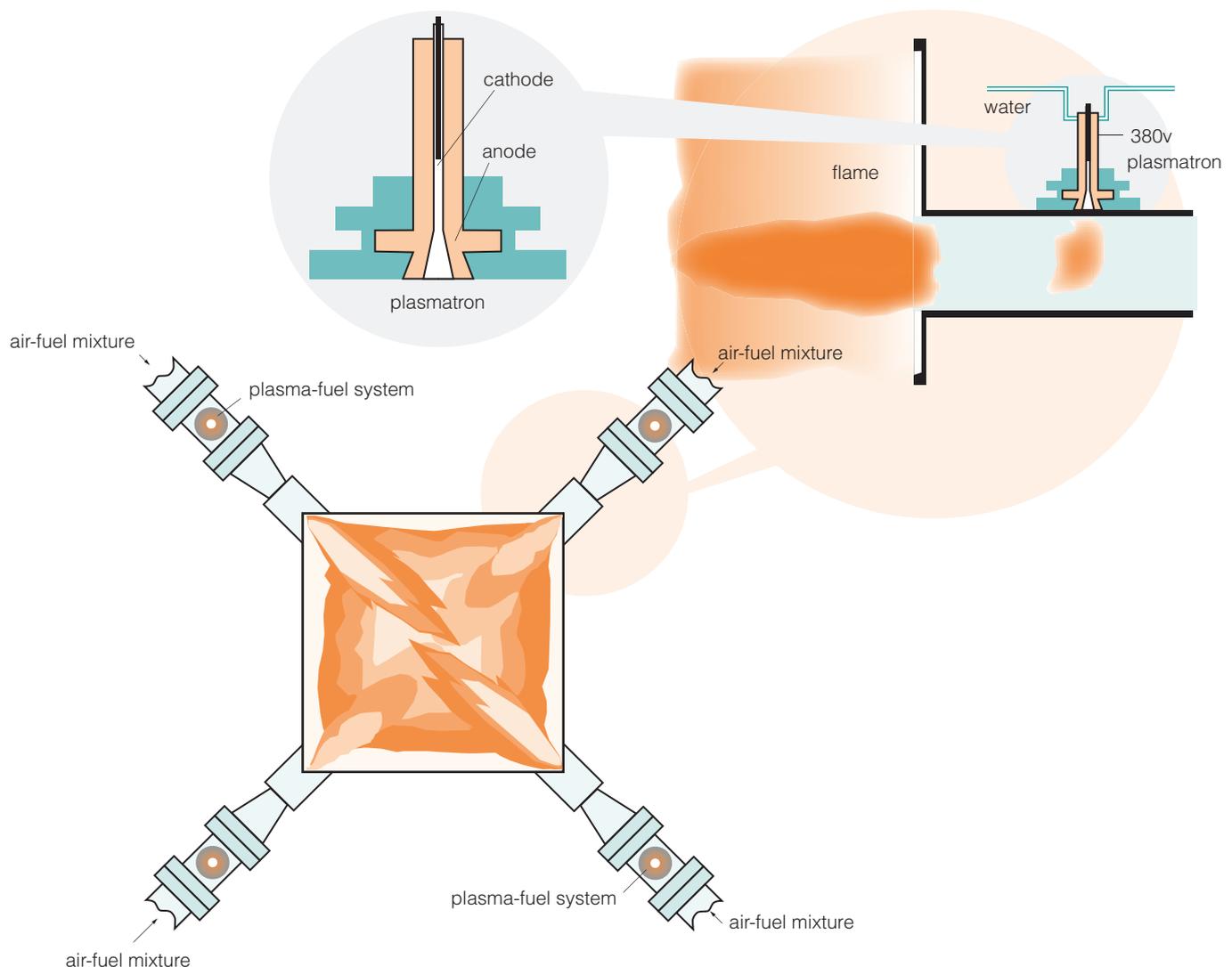


Figure 8 Schematic diagram of a plasmatron on a corner-fired PCC boiler (Gorokhovski and others, 2007)

enhancement. This plasma-supported combustion technology uses an electroarc plasma (plasmatron) to pre-process a portion of the pulverised coal prior to the combustion of the majority of coal in a furnace. During the pre-processing, the plasmatron induces gasification of the coal and partial oxidation of the char carbon, resulting in a mixture rich in CO and H₂ (50–70% by volume) (Gorokhovski and others, 2007). This highly reactive mixture of combustible gases (at a temperature of around 1000°C) can promptly ignite the main coal stream that is not plasma-treated, creating a stable main flame. The operating principle of plasma fuel systems (PFS) is illustrated schematically in Figure 8. As soon as the combustion of the main coal stream is stabilised, the plasma flame can be switched off and the PFS then operates as a normal PC burner. PFS can be switched on again in the case of an unstable flame or during boiler start-up.

The PFS can effectively reduce the unburnt carbon by nearly 75% from a 4% level and the reduction increases with the specific power consumption of the PFS (Gorokhovski and others, 2007). The specific power consumption is defined as the ratio of plasmatron electric power to the pulverised coal treated in the PFS. The reduction in unburnt carbon is considered to be the increase in the reactive surface area of coal particles due to the heat-shock imposed by the arc plasma and consequent fragmentation of coal particles.

There are a number of additional advantages of using the PFS. The most prominent advantage is the oil/gas-free start-up of PCC boilers, which is not only faster but also less costly. Gorokhovski and others (2007) considered that PFS consumes only 5–25% of the calorific power of treated coal compared to about 30% when fuel oil is fired to start up a boiler. It is estimated that since 1995 more than 20,000 t of fuel oil has been saved in the Gusinozersk thermal power plant in Russia (Gorokhovski and others, 2007). The oil/gas free start-up also results in a reduction in the emissions of NO_x and sulphur oxides, carbon monoxide and vanadium pentoxide of some 13,000 t/y in the Gusinozersk plant. In addition to a more reliable flame stabilisation, PFS can ensure a stable liquid slag yield along with liquid slag removal. This plasma-supported coal combustion enhancement technology has been successfully tested and restricted on 27 PCC boilers in seven countries (Russia, Kazakhstan, Korea, Ukraine, Slovakia, Mongolia and China); this technology already has more than 400 applications on boilers in China (Gorokhovski and others, 2007).

Based on an evaluation at the US DOE, the plasma technology may not be effective on coals with very high moisture. Also, the reductions in NO_x and sulphur dioxide emissions have not been substantiated (US DOE, 2010).

3.6 Computer-based combustion optimisation tools

Computer-based combustion optimisation provides a means to reduce NO_x emissions without compromising carbon-in-ash. Since optimisation of coal combustion in full-scale boilers involves adjustment and balancing of many factors (as discussed earlier in this section), it is extremely difficult to do

manually. However, increasingly powerful computers have made the job easier and more efficient. The availability of plant operating history data from digital control systems (DCS) in many existing plants also provides a greater understanding of what occurs in a boiler. These data can be used in plant models or simulators to help optimise combustion performance and reduce NO_x emissions. Using computer-based optimisation systems in coal-fired power plants is discussed in a previous IEA Clean Coal Centre report (Soud, 1999). Plant combustion simulators are discussed by Niksa (1996), Peltier (2002) and Lee and others (2000). This section focuses on combustion optimisation tools with specific capabilities for unburnt carbon reduction. These tools can be broadly divided into three categories: expert systems, neural network systems and coal combustion simulation.

3.6.1 Expert systems

An expert system acts as an on-line database to help operators make sense of what the system output is informing them about the combustion process in the furnace. It can also act as automatic fault detection, diagnostic and correction systems (Soud, 1999). Zonal™ and PECOS™ are typical expert systems and are introduced briefly.

GE Energy Environmental Services provides the Zonal™ system for on-line control of unburnt carbon, which comprises a burner coal flow balancing function and a combustion tuning function (Widmer and others, 2005). Zonal™ combines continuous coal flow monitoring and automated adjustable coal flow dampers to optimise coal flow distribution to burners. Coal, due to its greater density and momentum, tends to be distributed less evenly than air among burners, leading to uneven spatial combustion. It is difficult to correct significant imbalances in spatial combustion by adjusting air distribution alone. GE therefore proposed a two-step process to correct such imbalances. Coal flows among burners are first roughly adjusted using dampers to attain better fuel distribution among burners. A brief introduction to adjustable coal flow dampers can be found in a DTI report (2001). The burner air flow is then trimmed to respond to variations in spatial combustion performance. It was reported that the two-step control process was able to balance coal distribution within the ± 5% target and maintain the balance over time and against varying mill output.

The model-based combustion tuning function analyses information from on-line CO and O₂ sensors and correlates poor combustion regions to specific burners. These sensors, installed in the upper convective backpass elevation of a boiler, overcome the difficulties of making direct burner throat airflow measurement, and traces poor combustion zones to specific burners and OFA ports.

GE's Zonal™ system has demonstrated its ability to manage carbon-in-ash without raising total boiler excess air levels or increasing NO_x emissions. Balanced spatial combustion through combustion tuning at the burner levels effectively reduces both high CO concentration zones and the overall unburnt carbon level. Other benefits include reduced average

and peak furnace exit gas temperatures, reduced tube metal thermal fatigue and soot blowing. All these benefits combine to reduce slag formation and tube wall degradation, leading to lowered boiler heat rate and increased boiler availability.

PECOS™ (Plant Environmental and Cost Optimisation System), developed by Praxis Engineering, Inc., is an expert system that considers a power plant in its entirety. Its basic goal is to minimise the controllable costs of power generation by performing on-line analysis of all operational components and their co-optimisation to achieve a minimum generation cost. As a modular software, PECOS™ can be installed with individual modules chosen by users. Installation of PECOS™ is uncomplicated and does not need to be done during a boiler outage. It has modules to acquire data from any of a variety of plant data systems including DCS, programmable logic controllers (PLC), plant data logger and data highway. PECOS™ is a distributed client/server application and thus can be used by anyone on the utility network. Its structure and integration to power plants have been reviewed by Soud (1999).

One of its sub-modules, CBAS™ (Coal Blend Automation System) is discussed here because it concerns coal selection and blending. CBAS™ is responsible for managing all stockpiling and blending actions in the utility yard. Its basic objective is to control and predict the quality of coal at the burners in realtime. For a power plant using coal from different sources, CBAS™ represents a relatively simple method to minimise fuel cost and to ensure a feedstock with a predetermined quality at all times. In contrast to using fixed blends in conventional practices, CBAS™ enables plant operators to dynamically change blends in realtime to respond to shifting conditions such as load, emissions, stack opacity, and coal availability/quality. It does so by the following mechanisms:

- tracking the sequence, quality and tonnage of coal being loaded into piles, silos or bunkers;
- using Praxis's proprietary Silo Flow™ model to characterise the complex flow of coal through stockpiles and silos/bunkers. As a result, CBAS™ can advise operators on making blending decisions in the yard such that feedstock of a predetermined quality can be delivered at selected times;
- Combining dynamic coal lending algorithms with knowledge of coal quality and plant conditions to simultaneously optimise combustion efficiency and NO_x emissions, and to tackle fuel-related problems such as increased stack opacity, fouling and high heat rate.

CBAS™ had been successfully installed on nearly 1000 units in the USA by 2000 (Soud, 1999). Similar expert systems for coal blending include CoalFusion™ developed by Ready Engineering, and ABB's KOFIS (coal flow information systems), which are not discussed further here. Interested readers can find more information on the provider's websites.

3.6.2 Neural network systems

A neural network system learns the relationships between plant operating conditions, performance parameters and

emissions through processing plant history operating data or a series of test data. This process is often termed the system training process, in which a neural network system develops a complex nonlinear function to map the system inputs to the corresponding outputs. This function can be used in a mathematical minimisation algorithm that finds the optimum operating conditions. Neural network systems are particularly useful for optimisation tasks involving a large number of example data, for which straightforward and fast rules cannot be applied easily. These systems require no complex coded programmes, tolerate loss/errors of some input data and are sensitive to varying process conditions. However, large and complete sets of data on plant operations are required to train a neural network system. An introduction to neural network systems and their application to coal-fired power plants can be found in an IEA CCC report (Soud, 1999) and a review article (Reinschmidt, 1994). Two typical commercial neural network systems for carbon-in-ash reduction are discussed as follows.

Boiler OP™ is an intelligent computer software which combines an expert system, neural networks and boiler optimisation algorithm into a single programme for tuning a boiler into optimised combustion. Boiler OP™ works by five steps:

- Boiler inspection (for example, convective pass leakage), fuel check (fineness, distribution among burners, for example), and instrumentation calibration;
- Setting up a database on plant operation by performing parametric tests (Boiler OP™ driven);
- Data correlation using the neural networks (Boiler OP™ driven);
- Using the correlation obtained to determine optimal solution (Boiler OP™ driven);
- Conversion of the optimal solution into control curves.

The expert system included in Boiler OP™ is used to carry out the requisite parametric tests. It recommends control settings for test points to the plant operator and the boiler control parameters are then adjusted. The test data are acquired by the plant's DCS for subsequent correlation analysis and also for determining each point in a test sequence. Boiler OP™'s testing approach is designed to minimise the time and expense of the parametric tests. Dependent upon the complexity of the boiler controls, approximately two weeks of testing is needed over a particular load range to acquire the requisite operating data to set up a sufficient database. The neural network then analyses the collected operating data and creates a model that Boiler OP™'s optimisation algorithm can use to find the best operating conditions for a desired objective. To this end, the optimisation algorithm recommends the best combination of control settings which undergo verification/checking for their applicability and plant safety.

Boiler OP™ can produce substantial savings due to reduced fuel consumption and heat rate. A 0.7 million \$/y cost saving was achieved for a 600 MW coal-fired unit when the heat rate was reduced by 95 MJ/kWh (Soud, 1999). Additional savings can be produced if the optimised plant performance avoids installation of expensive low NO_x burners, eliminates unit derates due to clearer stack opacity and enables ash sales if carbon-in-ash is minimised.

The current version of Boiler OP™ can be used on both corner-fired and wall-fired PCC boilers with either conventional burners or low NO_x burners plus OFA. With minor modifications to the software, it can also be used for boilers with SNCR (selective non-catalytic reduction) systems (Soud, 1999). Boiler OP™ has been implemented at more than 24 US power plants since the mid-1990s; its first implementation on a Chinese utility unit, the 600 MW Pan Shan power plant located nearby Beijing, was completed in the spring of 2009 (Pfitzer, 2009).

GNOCIS™ (Generic Neural Optimisation Control Intelligent System) Plus is the latest software package offered by E. ON UK, which takes data from the existing control system of a power plant to calculate optimal control settings for reduction of NO_x emissions, carbon-in-ash and heat rates automatically. Operational constraints can be included in the calculation, for example engineering limits on burner tilts. GNOCIS™ Plus can be used either in the open-loop mode that only provides advisory information to the plant operator, or in the closed-loop mode that automatically changes plant settings to achieve the desirable output. GNOCIS™ Plus consists of three key components: the on-line learning capability, the ‘what-if’ prediction capability and the optimisation capability. It incorporates the following neural network features:

- online system retraining feature (adapt continuously to plant changes, such as those resulting from different fuels or major plant outage, with no need to rebuild models periodically);
- selection of optimisation parameters and robust optimisation algorithms;
- plant constraints accommodation;
- flexibility in being configured for various plant designs and pollution control equipments.

GNOCIS™ Plus can advise on optimum settings for mill biasing, excess air, SA/OFA airflow dampers opening and burner tilt if available. The benefits gained from GNOCIS™ Plus are site specific, but the average reduction in NO_x emissions of 10–15% and plant efficiency improvements of 0.2–1% can be expected (Piazza, 2003). A reduction in LOI by approximately 3% has been reported in trials undertaken at the Gaston Unit 4 of Alabama Power (Soud, 1999). A payback period of one year is generally estimated for a power plant. There are over 50 active or planned GNOCIS™ installations representing more than 25 GWe of generating capacity in the USA (Soud, 1999). Several power plants across Europe have installed the GNOCIS™ Plus system, including the 320 MWe Vado Ligure power plant in Italy, 2 GWe Kingsnorth power plant and 2 GWe Ferrybridge, Fiddler’s Ferry and West Burton power plants in the UK (Piazza, 2003). An installation was also constructed in China at a 300 MWe power plant in the southern coastal Guangdong province (Modern Power System, 2007).

3.6.3 Coal combustion simulation

Coal combustion simulation has been developed extensively over the past three decades. It can be used as a predictive or design tool and complement other experimental techniques as discussed earlier for improving coal combustion in full-scale

PCC boilers. The backbone of coal combustion simulation is the coal combustion model, which is available either as a stand-alone package or as a component of a comprehensive boiler model. Most recently, there is a trend to combine Computational Fluid Dynamics (CFD) tools, which model the turbulent furnace environment, with some advanced models of specific mechanisms involved in coal combustion in full-scale boilers. It is beyond the scope of this report to elaborate on coal combustion modelling, which is a complex subject in itself. Interested readers can find more detailed discussion in the references quoted in Table 1 and others (Field, 1970; Khan and others, 1971; Baum and Street, 1971; Williams and others, 1994; Elston, 2003; Backreedy and others, 2006a and b; Pallarés and others, 2007). Nevertheless, this section briefly introduces the typical process of coal combustion simulation and discusses how the simulation can help resolve the carbon-in-ash issue.

Typical simulation process

A typical coal combustion simulator must include mechanisms to describe major flows through a furnace, particle dispersion into the flows, turbulent mixing of gas-phase reagents, coal devolatilisation, combustion of volatiles and CO, char oxidation, NO and SO₂ formation, and radiation (Niksa, 1996). Table 1 lists the major mechanisms used in reported coal combustion models/simulators and their corresponding treatment submodels or approaches. Their detailed description can be found in the references quoted.

Generally, the first step of coal combustion simulation is to describe the complex turbulent conditions within a furnace. To this end, differential equations for the conservation of species, momentum and energy (enthalpy) are solved using empirical turbulence models. The most popular turbulence model is the K- ϵ ; K denotes the turbulence kinetic energy and ϵ denotes the turbulence dissipation rate. Other second-order turbulent models, such as Reynolds stress models or algebraic stress models, work no better than the K- ϵ model, particularly for burning jets in full-scale boilers (Niksa, 1996).

After the turbulent conditions of the furnace are determined, the next step is to calculate the temperature field within the furnace by considering radiation and the heat losses through the furnace wall. No simulation has yet attempted to resolve heat transfer by convection in detail. Loading of soot strongly affects the radiation, so it is taken into account in some submodels. Grey-body assumption is generally used in nearly all coal combustion simulations although it may overestimate incident radiant fluxes by about 10% and misrepresent the relative contributions from various particle types (Niksa, 1996).

Particle flow in the furnace is the next simulation task. As particle suspension becomes very dilute once the particles enter into the burner throat and mix with combustion air streams, there are no appreciable interactions among individual particles. This discrete particle transport is exploited to model the complete combustion histories and trajectories of individual coal particles. Usually a few thousand particle trajectories are assigned per simulation. The oxygen concentration surrounding a coal particle and its surface temperature can be derived from the temperature and flow profiles determined in preceding steps. These data are

important inputs for the subsequent modelling of coal devolatilisation, volatiles combustion, char combustion, and/or pollutant formation. The associated changes in the free-stream oxygen concentration and particle temperature will be calculated as coal combustion proceeds; the calculation iterates until the model converges. The effect of turbulent gas flows on particles is generally accounted for by a particle-source-in-cell submodel or particle dispersion submodels (Niksa, 1996). The latter is based on either

stochastic random-walk simulations such as Lagrangian momentum balance and Monte Carlo simulation, or empirical particle diffusion velocity. The converse effect of particle motion on the gas flow is either neglected or implemented with empirical correlations. Particle motion in a turbulent two-phase field is a complex subject where many basic mechanisms are still not well understood. Even the turbulent gas flow can be accurately depicted, particle motion is still subject to many other uncertainties.

Table 1 Mechanisms in reported models of coal combustion in full-scale coal-fired boilers and their corresponding submodels/treatment approaches

Mechanism	Submodels or treatment approaches
Turbulent flow field	(1) K- ϵ (2) RNG(re-normalised group) K- ϵ [to account for the effects of smaller scales of motion] (3) RSM (Reynolds Stress model) [second-order closure model working better for cold swirling jet flows; but proves not better than K- ϵ for burning fuel jets]
Particle dispersion (Niksa, 1996)	(1) Lagrangian momentum balance (2) Empirical diffusion velocity (3) Monte Carlo simulation
Mixing (Niksa, 1996)	(1) EBU (empirical eddy-break-up model) (2) EDIS (empirical eddy dissipation model) (3) Mixture fraction – PDF (probability density function) method
Devolatilisation	(1) Global kinetic model (Wu, 2005) SFOR (single first-order reaction) C2SM (two-step competitive reaction) DAE (distributed activation energy) (2) Empirical model (Niksa, 1996) T-ramp (linear function of particle temperature) EVAP (evaporative rate) (3) Network model (Wu, 2005) FG-DVC (functional group – depolymerisation vaporisation cross-linking) CPD (chemical percolation devolatilisation) FLASHCHAIN
Volatile combustion (including CO oxidation) (Niksa, 1996)	(1) EQ at MR: conversion to equilibrium products at the rate of mixing of volatiles and oxygen) (2) Min (FR, MR): the slower of the mixing rate and a global kinetic rate expression
Char oxidation (Niksa, 1996; Wu, 2005)	(1) Global reaction model (based on apparent activation energy; the overall reaction rate consists of two elements : the diffusion rate coefficient and the chemical reaction rate coefficient) (2) Intrinsic reactivity model (based on the intrinsic reactivity of char and linked to the film diffusion mechanism, that is, the oxygen partial pressure at the particle surface)
NO production (Niksa, 1996)	(1) D2SM (competitive channels for conversion of HCN into N ₂ or NO, proposed by DeSoete (1974)) (2) Extended Zeldovitch mechanism for thermal-NO (3) Conversion of Char-N into NO and/or HCN (4) Reduction of NO by hydrocarbons (5) Reduction of NO on char (6) prompt NO: conversion of N ₂ to NO by hydrocarbon radicals
Radiation (Niksa, 1996)	(1) Discrete ordinates method (2) Discrete transfer method (3) Non-equilibrium diffusion method (4) N-flux method (5) Monte Carlo simulation
Char fragmentation	Percolation theory (Liu and others, 2000)

Modelling the combustion of pulverised coal particles is the core of any coal combustion simulation. Three aspects need to be included, which are devolatilisation, combustion of volatiles and char oxidation. Devolatilisation is crucial during which coal mass breaks down into volatiles and char. Important parameters are the true volatile yields (rather than the values in proximate analyses), the devolatilisation rate and reactivity of the resulted char. These parameters generally need to be determined in high temperature experiments in, for example, a drop tube furnace or a wire-mesh apparatus. The widely-used devolatilisation submodels are summarised in Table 1. Global kinetic submodels are relatively simple and regularly incorporated in many commercial CFD codes. T-ramp and EVAP submodels are also empirical and less popular. All those submodels are actually curve-fit approaches, so experiments are required to determine some key parameters and the analyses need skilled modellers (hence results are subjective). Moreover, volatile compositions are not resolved into molecular products, but are based on the measured elemental compositions of the original coal or resulted char. More comprehensive devolatilisation models are FG-DVC, CPD and FLASHCHAIN. They can predict the volatiles release rate, volatile composition (tars, gases and char), and the concentrations of key species affecting the porous structure of the resulting char. FG-DVC and CPD have a scientific basis with the option of inputting data from advanced chemical characterisation techniques such as nuclear magnetic resonance (NMR) analysis. FLASHCHAIN involves a complex correlation approach based on a large range of experimental data.

Volatile combustion is a complex phenomenon. The complexity lies in both the fluctuating quantity of participating species, their cross-correlations and the varying local temperature. It is therefore difficult to describe the burning rate in defined mathematical terms. Alternatively, nearly all coal combustion models make a drastic assumption: all chemical reaction rates in the gas phase are assumed to be fast enough to achieve thermochemical equilibrium at the pace of mixing rates. In other words, volatile combustion submodels determine the equilibrium composition of the combustion products (satisfying Gibbs free energy minimisation) from the elemental composition of volatiles. Consequently, the burning rates can be approximated by the mixing rates of secondary air with volatile-rich zones. This assertion may be plausible for near-stoichiometric hydrocarbon oxidation at high temperatures, but is certainly not valid for lean/rich hydrocarbon mixtures, CO oxidation, or NO formation. Mixing rates for volatile combustion are usually evaluated with either the eddy break-up/dissipation model (Lockwood and Romo-Millares, 1994; Mann and others, 1995) or a probability density function (PDF) with respect to mixture fractions (Niksa, 1996).

Char oxidation is much slower compared to devolatilisation and volatile combustion. The rate at which heterogeneous char oxidation proceeds largely determines the extent of carbon burnout. Under pulverised coal firing conditions, char oxidation is considered to occur after volatile combustion has completed because gaseous fuel surrounding char rapidly consumes available O₂. Char oxidation models can be broadly classified into two categories: global reaction model and

intrinsic reactivity model (Wu, 2005). The global reaction model is based on the apparent activation energy, predicting the overall surface reaction rate of a char particle. The global reaction models proposed by Field (1970) and that by Baum and Street (1971) have been widely used. More complex global reaction models are CBK (Hurt and others, 1998) and the IFRF enhancements to the Field model (Elston, 2003).

The Carbon Burnout Kinetics (CBK) model is a kinetics package that integrates the global char oxidation model of Mitchell and others (1992) with deactivation submodels for thermal annealing and ash inhibition (Hurt and others, 1998). It can predict the rate of burning, the char particle temperature, and the changes in coal particle diameter during combustion. It comprises the following four key submodels:

- a core code combining the single film treatment of char oxidation with rank dependent kinetic correlations;
- a submodel accounting for statistical variations in single-particle reactivity and density and their implications;
- a submodel accounting for thermal char deactivation/thermal annealing;
- a physical property submodel describing swelling, diameter/density changes during combustion, and ash inhibition in the late stages of combustion.

CBK8 is the latest CBK version. It incorporates mass-specific intrinsic kinetics, a simple model of the reaction/diffusion process within porous char particles, and the single-film description of the boundary layer. It is able to predict burning rates over a wide range of conditions, including Zone I, Zone II, and Zone III and their transition regimes. As an option, it offers the function of using standard fuel analytical data to estimate key input parameters through fuel-general correlations. CBK8 also provides a better description of extinction phenomena by taking into account the effect of ash on heat transfer in the late stages of char burning.

In global reaction models, a number of Arrhenius type parameters need to be determined experimentally, which is a time-consuming and sometimes difficult task. Conversely, intrinsic reactivity models are based on the intrinsic activation energy (35–40 kcal/mol) for carbon-oxygen reactions which is the same for all coal chars. In principle, only basic coal analytical data are required as input into intrinsic reactivity models. Generally, the effect of oxygen diffusion is reflected by the oxygen partial pressure on the char particle surface. Other factors affecting the apparent reactivity of a char include its initial reactive surface area and subsequent variation during combustion, particle density, the concentration of reactive sites, ash content and any catalytic effects. All these factors are linked with the pre-exponential factor in an intrinsic reactivity model. The most noteworthy development in recent years was made at the University of Leeds, UK (Williams and others, 1994; Elston, 2003; Backreedy and others, 2006a and 2006b; Pallarés and others, 2007). The Leeds model takes into account swelling, variation of surface area with the degree of reaction, thermal annealing, ash inhibition and effects of maceral composition.

Pollutant formation is generally the last task in a coal combustion simulation. All the organic sulphur will be released during devolatilisation under typical pulverised coal

firing conditions. Ultimately, all gaseous sulphur species will be converted to SO_2 under oxidising conditions. SO_2 formation is therefore a simple modelling task. In contrast, NO_x formation is very complex, with tars, soot, char and gaseous species (such as HCN, NH_3 , N_2 and NO) all playing their respective roles. To simplify the problem, only NO formation is considered in coal combustion modelling; it is assumed that all nitrogen in coal is converted to HCN during devolatilisation. The rate of NO formation is determined by competition of HCN conversion into NO or N_2 . The rate parameters can be assigned empirically using the DeSoete (1974) approach for all coal types.

Applications of Coal Combustion Simulation

Coal combustion simulation is a versatile tool used to address the carbon-in-ash issue. Firstly, it is a diagnostic tool that identifies and characterises the most important operating conditions linked to excessive carbon-in-ash. The most notable studies in this respect are those made by Professor Kent's research group at the University of Sydney, Australia.

In their simulation of a 410 MW tangentially-fired furnace with a six-level burner manifold (see Figure 9a), they found that coal particle trajectories moved towards the bottom ash hopper (Luo and others, 1991) and then extinguished (Chen and others, 1992). The predicted levels of carbon in bottom ash were therefore double those in the flue (Luo and others, 1991). Although these particular simulations were never validated against any measured data, a similar study did provide indicative evidence. Predicted levels of carbon in bottom ash from a 200 MW tangentially-fired furnace under four sets of operating conditions agreed well with the measured values (Chen and others, 1992). As the reported unburnt carbon levels from full-scale furnaces are invariably based on flue-stream samples, this finding suggests that carbon burnout in the furnace may be overestimated. In addition, other potential causes of excessive carbon-in-ash were identified as follows: biased coal flows among the burners, coal particles of top-grind sizes, and high coal particle concentrations near furnace walls. The last cause can be observed clearly in Figure 9b where centrifugal forces

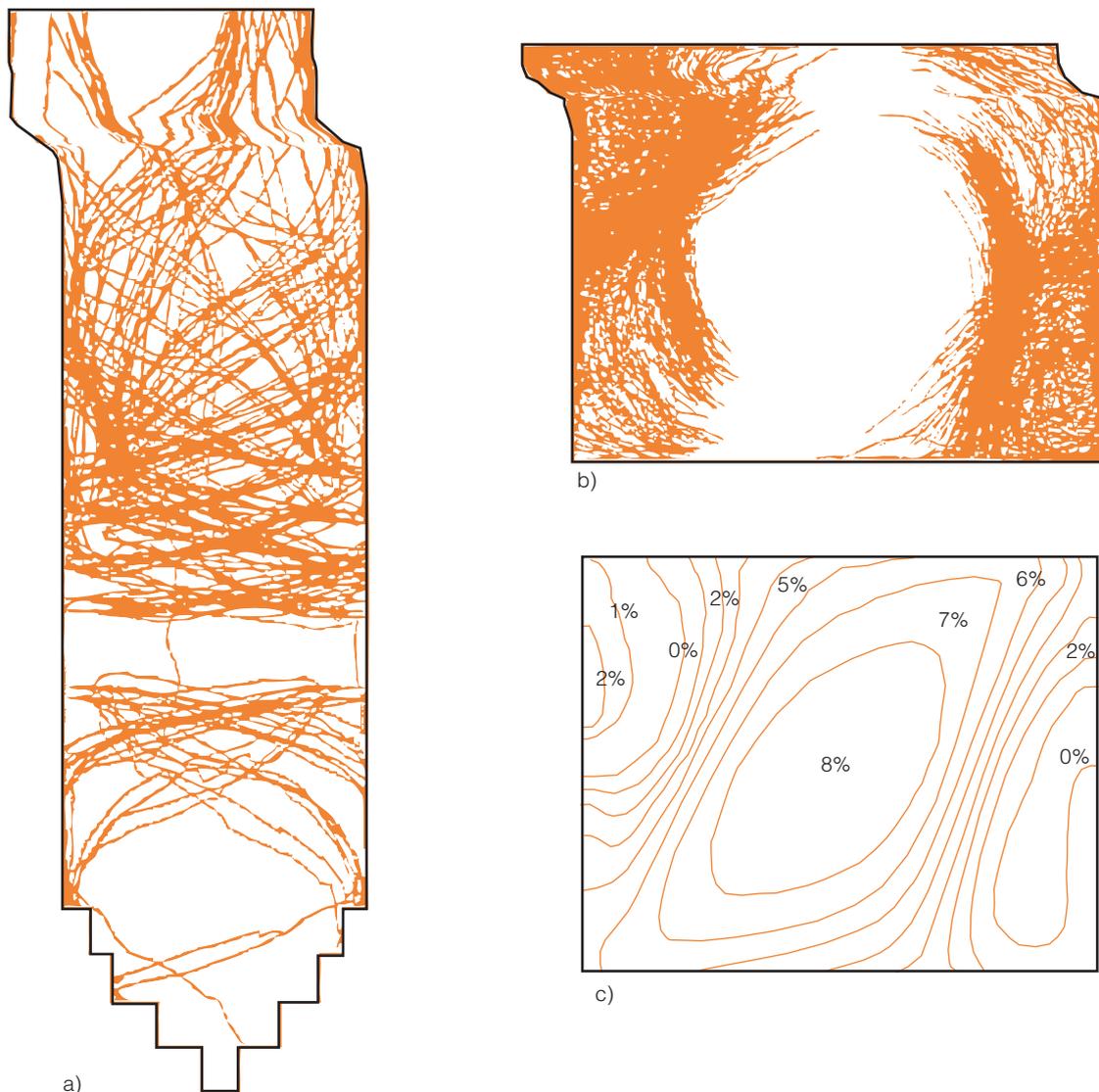


Figure 9 a) Simulated particle trajectories throughout a 410 MW tangentially-fired furnace (Chen and others, 1992); b) particle trajectories in the cross-section 10 m from the top burner elevation (Mann and Kent, 1994); c) distribution of O_2 mole fractions within the cross-section 5 m from the top burner elevation (Mann and Kent, 1994)

divert coarser coal particles towards the walls. This depletes the local O₂ concentrations (*see* Figure 9c) and consequently slows the char oxidation rates, promoting carbon carryover. O₂ depletion in these regions indicates the importance of char gasification with other reagents to overall carbon consumption; calculations taking into account char gasification by steam and CO₂ have predicted less unburnt carbon (Mann and Kent, 1994).

Once the basic causes of excessive unburnt carbon have been identified, coal combustion simulation can be used to assess the efficacy of adjusting a certain factor to improve carbon burnout. The relative importance of these factors can be ranked by regulating and characterising closely each one in a series of test burning simulations, then collating these simulated results to see how they match the observed values (Chen and others, 1992). For the 410 MW tangentially-fired furnace mentioned above, maldistribution of coal among burners was found to be the dominant factor, while top grind size and high particle concentrations near furnace walls were relatively less influential.

Finally, coal combustion modelling can assist plant operators in identifying the most cost-effective control strategies by ranking their benefits. Taking again the 410 MW tangentially-fired furnace for example, the burner tilt angles were important, given the close correlations among particle trajectories and the unburnt carbon levels. The amount of coarse coal particles pushed towards the furnace walls was effectively reduced by pointing the burners more toward the centre. This led to 1.5% increase in the combustion efficiency. Biasing more air to the lower row of burners, from which coarse coal particles tended to enter the bottom hopper, could result in half of this gain. About 0.2% further gain could be realised by making the coal flow distribution more balanced among all burner elevations or by biasing the air flows into one of the diagonals across this furnace (Boyd and Kent, 1994).

Coal combustion modelling has demonstrated its particular ability to limit the increase in carbon-in-ash resulting from retrofitting low NO_x systems to existing furnaces to comply with tighter regulations on NO_x emissions. In a recent European Commission project 'Minimisation of Impact of Nitrogen Oxide Reduction Technologies on Operation and Performance' (MINORTOP), the impacts of air staging, fuel properties, blends, coal particle fineness and temperature on the carbon-in-ash level have been assessed (Whitehouse and Riley, 2008). Key problems were identified for coals with low ash content or coals for which reactivity was particularly

sensitive to oxygen. Coal burnout was found to increase with increasing temperature, although no clear correlation was found between the extent of burnout increase with temperature rise. Tests also showed that the carbon-in-ash level increased with overfire air, but again no simple correlation was found. CFD simulation was made for a wall-fired boiler geometry using both laboratory- and pilot-scale data. An analysis of the particle fineness effect showed that particles of all sizes were present at the furnace exit in the case of simple staging conditions, whereas under non-staging conditions only coarse particles were present and contributed to carbon-in-ash. This means that, for non-boosted combustion, carbon-in-ash is very sensitive to the firing pattern. For boosted combustion, a high mixing of overfire air and char particles is key to uncompromised carbon-in-ash levels.

A fine tuning approach, developed by RJM International to optimise existing low NO_x systems on power plants, is also based on coal combustion simulation with CFD (Goldring, 2008). This solution-based approach focuses on getting the maximum performance out of existing equipments, instead of changing or modifying some critical and expensive components. The approach starts with a programme to capture baseline data from around 200 key points throughout a power plant when it is operating at maximum continuous rating for several hours. This establishes exactly what is going on at each stage of the operation, from the pulverised coal delivery via mills and classifiers, right through to flue gases exiting the stack. The captured baseline data are then fed into a proprietary CFD simulator, which mirrors the way in which the plant operates. Parameters are then adjusted until the simulated plant performance matches the actual measured plant data. In this way, a virtual version of the plant can be established. The virtual plant can subsequently be used to assess the impact of a number of changes on key plant operational targets such as NO_x emissions, boiler efficiency and carbon-in-ash. This approach has been recently used in an emission reduction project at the dual fuel AES Kilroot plant in Northern Ireland (Goldring, 2008). It successfully defined the orientation of a distribution device added in the coal pipe to each burner to break up the coal stream rope. This particular orientation would not have been chosen if the actual visual CFD data had not been available. Furthermore, the simulator enabled the plant operators to design and test the air baffles required to distribute the air evenly to the burners, which was otherwise difficult to undertake manually due to the complexity of the airflow delivery system in the plant. The NO_x and carbon-in-ash reductions achieved at Kilroot are shown in Table 2.

Table 2 NO_x and carbon-in-ash reductions at Kilroot (Goldring, 2008)

	LCPD and contract targets	Prior-project plant performance data	Post-project plant performance test data
NO _x , firing South Africa coal, mg/m ³ (6% O ₂ dry)	500	648	444; 31% reduction
NO _x , firing Colombian coal, mg/m ³ (6% O ₂ dry)	500	638	339; 47% reduction
Carbon-in-ash, firing South Africa, %	< 6.5	8	5.5; 31% reduction
Carbon-in-ash, firing South Africa, %	<6.5	4.1	1.25; 69% reduction

The reductions achieved at Kilroot have made a significant difference to the overall profitability of the plant. The changes made on Unit 1 delivered a 0.7% improvement in boiler efficiency. This equated to a potential annual saving of over \$700,000 at coal price of 200 \$/t, given that the unit consumed in excess of 0.5 Mt of coal per annum (Goldring, 2008). When the additional revenue stream yielded from saleable low-carbon fly ash and associated avoidance of ash disposal cost were factored in, the economic gain was significant.

Most recently, coal combustion modelling has been applied in the European Commission sponsored project “Development of a Carbon-in-ash Notification System” (CARNO) (Stephenson, 2007). A computer model, the CARNO Adviser, was developed as part of the project to predict the carbon-in-ash levels for a given coal and furnace set-up (including the overfire system). This CBK8-based burnout predictor serves the following two purposes: (1) it answers the question whether excessive carbon-in-ash is simply a consequence of burning a particular coal or plant operating faults; (2) if the carbon-in-ash is not fuel-related, it calculates the sensitivity of the unburnt carbon level to known plant conditions to determine what plant fault is most likely to be the cause. Plant faults that the CARNO Advisor can assess include mill malconditions, boiler in-leakage, uneven distribution of fuel and air between burners, the excess O₂ level, unusual particle size distribution and excessive furnace slagging. Validation tests have shown that the CARNO Adviser is capable of predictions within $\pm 50\%$ of plant measurements. Although further improvement in the measurement accuracy is desired, CARNO Adviser has been working distinctly better than the previous modelling tools. The calculated sensitivities to changes in plant conditions were found to be very dependent on the state of the plant. This implies that the sensitivity analysis have to be based on an accurate representation of the plant operation.

3.7 On-line carbon-in-ash measurement

On-line carbon-in-ash measurement is a useful tool to constantly monitor the quality of fly ash and coal combustion performance in a full-scale PCC boiler. Where possible, by using the information from on-line carbon-in-ash analysers in a signal feedback system, a plant operator can optimise mill setting, improve the coal burnout performance, obtain an early warning of any deterioration, prevent excessive fuel consumption, maintain low particulate and CO₂ emissions and ultimately improve the overall plant efficiency.

A variety of on-line carbon-in-ash analysers are now commercially available (*see* Table 3). These analysers can be broadly categorised into extractive or non-extractive systems, dependent upon whether the device extracts an ash sample from the flue duct for analysis. The majority of commercial analysers use intrusive sampling techniques, typically an isokinetic sampler, to remove a fly ash sample from the flue path. Most of the isokinetic samplers are based on the CEGRIT (Central Electricity Grit Sampler) sampling system originally developed by the UK Central Electricity Generation

Board (Coal R&D Programme, 1997). The extractive analyser can be sub-divided into direct and indirect measurement systems. Direct measurement systems use an operating principle similar to the standard loss on ignition (LOI) test, which is to oxidise the residual carbon to CO₂ and then measure the liberated CO₂ to provide a direct measurement of the carbon-in-ash level. Indirect systems, in contrast, use some other characteristics of the carbon-contained ash, such as light reflection, light or microwave adsorption, or changes in capacitance, to measure the carbon-in-ash level. These indirect techniques generally require site-specific calibration and may be dependent upon the coal type, whereas direct techniques are not subject to the effect of coal type. Indirect measurement systems, however, work at a greater frequency because they do not require accurate sample weighing or measurement of evolved gases. They are also of a much simpler design than direct measurement systems. Table 3 summarises both direct and indirect measurement systems. It can be seen that microwave-based techniques dominate the indirect measurement systems because they are claimed to be unaffected by coal types. In addition, Iowa State University (USA) has been actively developing a photo-acoustic technique for indirect measurement of the unburnt carbon (Brown and Weber, 2003).

Extractive systems have experienced unacceptable availability in some cases due to blockages in the samplers. The location of the samplers was also found to be important in achieving a representative sample, which is difficult due to stratification of the dust flows around the sampling point. All these factors make non-extractive measurement systems preferable from the perspective of equipment maintenance, measurement accuracy and measurement response speed. At present, two non-extractive measurement systems are commercially available. They are the FOCUS (Furnace On-line Combustion System) Unburned Carbon Module manufactured by Applied Synergistic and ABB’s Carbon-in-ash Instrument.

Operational difficulties experienced with on-line carbon-in-ash analysers vary from plant to plant; this variation reflects differences in boiler and burner design, coal and ash composition, operating practice and maintenance. Generally, operators have been willing to persist with the analyser system on which they have managed to achieve acceptable performance. This level of acceptance is governed by the perceived need for a regularly updated knowledge of the carbon-in-ash level on the plant in question. It is still necessary to minimise the time delay between measurement and translation into the actual carbon content so that boiler operators can undertake remedial actions as soon as possible. In this regard, non-extractive systems appear more promising.

3.8 Summary

This chapter discusses how to prevent excessive carbon-in-ash on full-scale PCC boilers. The challenge is to minimise carbon-in-ash without impairing NO_x emissions reduction. Available measures are based on understanding pulverised coal combustion. A cleaner coal not only improves coal mill performance, but also reduces the plant emissions. Improving the fineness of coal mill output by dynamic classifier is the

Table 3 Commercially-available on-line carbon-in-ash analysers

System	Manufacturer/ distributor	Operating principle	Typical sample size per run	Accuracy	Measurement cycle time
Extractive systems					
<i>Direct measurement</i>					
TEOM® Series 4200 Combustion Efficiency Monitor	Rupprecht & Patashnick Co Inc (USA)	Direct mass measurement and liberated CO ₂ measurement	5–10 mg	± 0.5%	12 min
HOT FOILTM LOI Instrument	Fossil Energy Research Corporation (USA)	Direct mass loss measurement	20–80 mg	-	7–10 min per run; 30 min for 3 replicate runs
<i>Indirect measurement</i>					
SEKAM	Clyde-Sturtevant (UK)	Capacitance	375 g	± 0.5% over 0–15% carbon-in-ash	2–10 min
On-line Carbon Analyser	Berthold Technologies GmbH & Co KG (Germany)	Microwave transmission – phase shift	–	–	3–4 min
CIFA350	Scantech Ltd (Australia)	Microwave resonance cavity	3g	± 0.5% for 0–6% carbon- in-ash; ± 1.0% for 6-15% carbon-in-ash	4–10 min
CAM/ADS	Stock Equipment Company (USA)	Microwave adsorption	5 g	± 0.5% of ASTM LOI up to 5% (absolute); ± 10% of ASTM LOI over 5% (relative)	2–15 min
RCA 2000	M&W Engineering and Production (Denmark)	Light reflection	18g	± 0.5% for 2–7% residual carbon; 0–20% measurement range	3-15 min
RCA MI 2200	M&W Engineering and Production (Denmark)	Microwave transmission- phase shift	18g	± 0.3% for 0–20% residual carbon	3–15min
Non-extractive systems					
Carbon-in-ash Instrument	ABB Group	Microwave resonance measurement; sample independent	N/A	± 1% absolute across duct width	1 s
MECONTROL UBC	Promecon USA Inc	Microwave resonance measurement; sample independent	N/A	± 0.6% absolute, based on 1 s for 0–10% residual carbon	5–10 min
FOCUS	Applied Synergistic, Inc (USA)	Radiation energy infrared imaging (using near infrared wavelength camera)	N/A	–	1 min

Mobility	Maintenance	Reference
Portable or permanent installation	<15 min once per week	R&P (2004)
Portable	low	FERCo (2009)
least transportable	low	Bindemann and Colechin, 1997
–	–	Bindemann and Colechin, 1997
permanent installation	blockage of sampler	Bindemann and Colechin, 1997
midium	regular replacement of filters	Stockequipment, 2009
–	certain items replaced every 3 months; general overhaul and recalibration made every 6 months	M&W, 2009a
–	–	M&W, 2009b
permanent installed	low maintenance	ABB, 2009
permanent installed	–	Promecon, 2009
medium	–	Bindemann and Colechin, 1997

most effective measure. In some cases, more reactive coal/blends may be used to increase coal burnout. To optimise coal combustion in a full-scale furnace, it is necessary to use as high as possible combustion air temperatures, to reduce air/coal distribution imbalance among burners, to increase air-coal mixing rates at both burner and OFA levels, to increase local oxygen availability and coal particle residence time before reaching the convective pass and to use combustion diagnostic tools. A plasma technology developed recently has shown the potential of achieving better ignition and a more stable flame for less combustible coals (such as low volatile bituminous or high moisture lignite), although its application is restricted to tests at just 27 boilers in seven countries. Finally, computer-based combustion optimisation using expert systems, neural network systems and coal combustion simulation is becoming an invaluable measure to tackle the carbon-in-ash issue.

4 Ash utilisation and regulations

Fly ash is the largest constituent of coal combustion products (CCP); it accounted for 66% of the 64 Mt of CCP in Europe according to the 2005 statistics of the European Coal Combustion Product Association (ECOBA) (Vom Berg and Feuerborn, 2007). If all the fly ash was disposed of in landfills, its sheer quantity would occupy vast areas of land. Furthermore, increasing environmental awareness and associated tightening regulations in many countries are making this conventional disposal approach more costly. In the USA for example, the American Coal Ash Association estimated that the fly ash landfill cost may reach 22–44 \$/t or even higher (ACAA, 2009a). Coal-fired plant operators are keen to utilise some of the fly ash produced in their plants to reduce fly ash disposal cost and extend the lifetime of ash ponds.

There is a variety of ways to utilise fly ash beneficially, including cement/concrete production, mining applications, structural fills/embankments, waste stabilisation, and agricultural applications. Fly ash use in cement/concrete is the predominant application, representing 55% of the fly ash used in the USA in 2007 (ACAA, 2007) and 41% in the EU 15 in 2004 (ECOBA, 2006). Moreover, ash use in cement/concrete also represents the most valuable utilisation option, which can be easily seen in Table 4. In contrast to the landfill cost of 22–44 \$/t, the sale of fly ash to the cement/concrete industry alone can create a significant profit stream. This explains why coal-fired plant operators are so concerned about the marketability of their fly ash. However, the sale of fly ash depends heavily on the location of the power plant generating fly ash and its distance from end users. Transportation costs must be low enough to make the overall ash price attractive for the users.

It should be noted that, apart from fly ash, bottom ash and boiler slag are also utilised in some cases. However, they are generally in low value applications, such as structural fills or pavement base. The absolute utilised quantity of the bottom ash and slag is also much lower than that of fly ash; for example, bottom ash only represented 9.6% and boiler slag

just 3.1% of total CCP utilised in the EU 15 in 2005 (Vom Berg and Feuerborn, 2007).

In this chapter, the impacts of unburnt carbon on the use of fly ash, particularly in cement/concrete production will be discussed. The relevant regulations on the permitted maximum level of carbon-in-ash in most coal-consuming countries are also reviewed. Thus the introduction of carbon reduction technologies outlined in Chapter 4 is kept in perspective.

4.1 Fly ash utilisation in cement/concrete production

The most profitable and largest use of fly ash is in cement/concrete production. Fly ash can be added to cement kilns to replace some of the costly raw materials such as shale and clay, thus saving natural resources. In some cases it is capable of altering the cement chemistry to improve the clinker quality. In this application, excessive unburnt carbon is of lesser concern because the carbon will eventually be consumed in the kiln (Goss, 2003). Actually, fly ashes with high carbon contents can serve as a partial fuel substitute to reduce the fuel consumption of cement kilns; for example, the Construction Technology Laboratories Inc in the USA has successfully demonstrated the use of fly ashes with loss on ignition (LOI) up to 21% in commercial cement manufacture (Bhatty and others, 2002). Nevertheless, careful adjustment to kiln operating conditions is required and the proportion of fly ash in the feedstock is generally no more than 15% (Bhatty and others, 2002).

Some good quality fly ash can be ground together with normal cement clinker to make blended cement; fly ash replacing 80% of normal clinker has been reported (Naik and others, 2003a). With reduced consumption of normal clinker for a certain cement output, production of blended cement can result in a significant reduction in CO₂ emissions. This is

Table 4 Typical price range of ash for various utilisation purposes (price ranges are converted from the reported price ranges on a short ton basis) (ACAA, 2009b)

Ash utilisation	Price range, \$/Mt
Cement and concrete use	
Concrete quality fly ash	22–50
Self-cementing fly ash	11–22
Self-cementing fly ash (for oilfield grouting or waste stabilisation)	17–28
Other use of ash	
Fly ash for flowable fill	>1
Bottom ash for snow and ice control	3–7
Bottom ash/fly ash for road base	4–9

because manufacturing of normal clinker emits a large amount of CO₂ as a result of calcination and fuel burning, estimated at 0.83 tonne of CO₂ per tonne of cement (80% clinker) in Europe (Cembureau, 1999) and 1.2 t/t in the USA (Deju, 2003). An approximate reduction of 1 tonne of CO₂ can be achieved when 1 tonne of normal cement clinker is replaced with fly ash. The greater fineness of fly ash also increases the grindability of the blended mix. The carbon-in-ash level, however, is a key factor to determine the suitability of a fly ash for making blended cement.

As a pozzolanic material, fly ash is used more widely as a substitute for cement in concrete production. There are a number of sound reasons for this utilisation of fly ash. First, fly ash is much cheaper than ordinary Portland cement. Transportation accounts for a large part of fly ash cost, so the price of fly ash is dependent upon the distance from the ash producing site. A typical price for fly ash in the Sydney market is 55 \$/t, compared to a typical price of 150 \$/t for ordinary Portland cement (Heeley, 2007). Reducing use of natural kiln raw materials and the associated reduction in CO₂ emissions, as mentioned above, can bring about environmental benefits. Fly ash can also improve the workability of the concrete produced due to the greater fineness of ash particles compared to clinker particles, which increases both the reactive surface area with free lime and ease of concrete flow.

Furthermore, the durability of concrete can be enhanced as the addition of fly ash provides improved resistance to chemical attack. Certain chemicals, mainly sulphates, present in cement clinker can react with free lime during concrete curing to cause expansive reactions and eventual failure of concrete work. Since fly ash can react with free lime, its addition to clinker/gypsum mixtures can consume most of the free lime, thus limiting the expansive reactions with sulphates. As fly ash is finer than cement, it can fill voids in concrete normally occupied by water so that water demand is reduced. This also helps to avoid segregation and bleeding in fresh concrete and improve its long-term strength. Fly ash can also reduce the expansive reactions between siliceous materials in concrete aggregates and alkali hydroxides in cement. This alkali silicate reaction (ASR) causes premature and severe cracking of the concrete. The reactive silica in fly ash combines with cement alkalis more readily than the silica in aggregates, and the resulting calcium-alkali-silicate gel is non-expansive. Fly ash is also effective in solving the ‘concrete cancer’ problem which results from corrosion of reinforcing steel due to reactions with chloride. The alumina content of fly ash can bind chloride and reduce its diffusion.

The environmental, economic, and engineering benefits make ash utilisation in cement/concrete desirable. However, excessive carbon-in-ash can render the ash unsuitable for use in concrete production, either in the form of blended cement or substitute for ordinary Portland cement.

4.2 Excessive unburnt carbon and use of fly ash in concrete

Excessive carbon-in-ash is known to adversely affect the

quality of concrete produced (Freeman and others, 1997). The uneven distribution of unburnt carbon may reduce the homogeneity of concrete and increase the internal tension that is often the cause of concrete cracks. Carbon’s dark colour may also be aesthetically unacceptable in certain applications. Nonetheless, the most prominent effect is the poor air entrainment performance during concrete production.

In many concrete formulations, air bubbles are intentionally entrained into the concrete mix through mechanical agitation and stabilised by the addition of specialised surfactants called air entrainment admixtures (AEA). These tiny air bubbles (<0.25 mm) form billions of microscopic cells in the concrete structure, which provide chambers for internal pressure release during the freeze-thaw cycles. Sufficient amounts of entrained air bubbles (typically 5–8% by volume) are hence important for the mechanical performance of set concrete.

However, the unburnt carbon can deactivate AEA significantly. Most of the AEA have a dual hydrophilic-hydrophobic nature and are surface-active in the aqueous medium of concrete mix. AEA stabilise air bubbles by, at the air-water interface, associating their hydrophobic ends with the air and orienting their hydrophilic ends into the aqueous phase, which are probably adsorbed on the surface of cement particles (Rixom and Mailvaganam, 1986). The bridging action of AEA stabilises the air bubbles, and also provides a network structure incorporating the cement particles and the air bubbles. Since AEA’s hydrophobic ends can react easily with the carbon surface, little active AEA would remain to stabilise the entrained air bubbles if the ash contains excessive amounts of unburnt carbon. Increased doses of AEA are required to obtain desirable amounts of entrained air bubbles. In addition to the apparent rise in cost, large fluctuations in the trapped air content may occur, given the inevitable heterogeneity of fly ash and variation in boiler operation. This will lead to inconsistent mechanical properties of the concrete produced.

In addition to the absolute quantity of unburnt carbon, its morphological form also affects its effectiveness in deactivating AEA (Rixom and Mailvaganam, 1986; Maroto-Valer and others, 1999). This is apparent in Figure 10 whereby at the same LOI level, fly ash from different sources present distinct air entraining performance (Hill and Folliard, 2006). Two lower-carbon ashes from Source 5 and 6 actually have the poorer performance. The surface area of mesopores (2–50 nm in nominal diameter) and macropores (>50 nm) is considered to be the reactive surface contributing to carbon-AEA reactions. For example, inertinite particles with mesopores accounting for approximately 90% of the total particle volume are more effective in deactivating AEA than isotropic coke (mesopores 70–80%) and isotropic coke (mesopores <60%) (Maroto-Valer and others, 1999). Although it is clear that the unburnt carbon quantity alone is not sufficient to judge the suitability of a fly ash for use in concrete production, the importance of unburnt carbon properties has not been recognised in most of the present-day regulatory standards for ash utilisation. The fly ash marketers have to resolve this issue through testing on a frequent basis, say hourly. The test results are supplied to the concrete producers who can adjust the dosage of air-entraining admixtures to ensure the finished concrete has the right

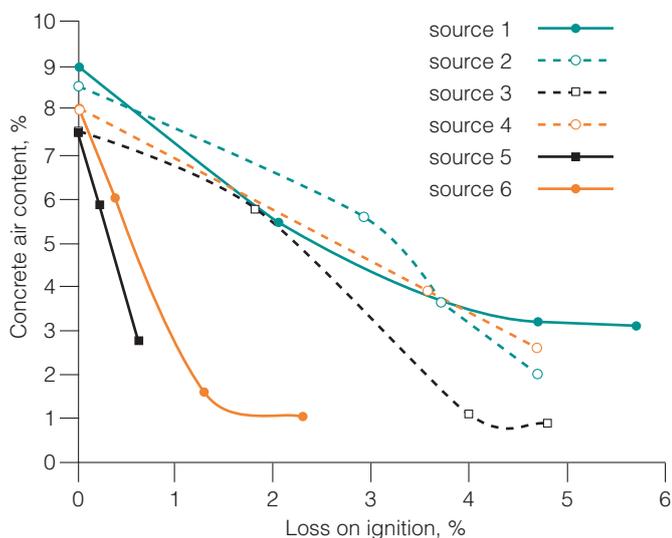


Figure 10 Impact of LOI on air entrainment performance for various fly ashes (Hill and Folliard, 2006)

amount of air bubbles trapped. This practice echoes the widely advocated ‘performance-based’ specifications for coal fly ashes.

4.3 Carbon-in-ash regulations

The carbon-in-ash level must be quantified and checked against the regulatory permitted range to enable effective selection of fly ash for use in cement/concrete. In practice, the loss on ignition (LOI) is widely used to indicate the unburnt carbon content of fly ash. LOI is the weight loss percentage after an ash sample is burned under standard conditions as specified in, for example, the ASTM C 311-77 and the EN 196-2:2005. The unburnt carbon accounts for almost all of the weight loss with oxidation of sulphur and ferrous compounds contributing the rest. The true content of unburnt carbon is typically 85–90% of the LOI value determined (Innogy, 2003).

The carbon-in-ash regulations, stipulating the permitted LOI range for fly ash utilisation, in major coal-consuming countries are summarised in this section. For countries where

data are available, the status quo of ash production and utilisation are also discussed.

4.3.1 Australia

Approximately 14.5 Mt of coal combustion products (CCP), mainly consisting of fly ash, were produced in Australasia (Australia and New Zealand) in 2007. About 30% of these CCP (4.308 Mt) has been utilised effectively; 1.504 Mt was used in high value-added applications, such as cement/concrete production, resulting in more than 1.2 Mt of CO₂ being abated due to a reduced requirement for clinker manufacture. The accumulated CO₂ reduction over the period 1975-2007 reached about 18 Mt as a result of substitution of fly ash for normal clinker (ADAA, 2009a).

Most of the fly ash produced in Australian power plants is categorised as Class F ash according to ASTM 618 because it has high silica and alumina content (80–85%) and low calcium content (CaO <10%) (ADAA, 2009b). Therefore, the fly ash is used primarily for partial replacement of ordinary Portland cement in concrete production. Its light to mid-grey colour is another advantage for this application. The first use of fly ash to replace Portland cement dated back to 1958 in the construction of Keepit Dam in New South Wales (Stafford, 1962).

In Australia the regulations on fly ash use in concrete are given in the AS 3582 series of standards ‘Supplementary Cementitious Materials for Use with Portland Cement’ (ADAA, 2009c). These standards stipulate that fly ash can account for 20–40% of total combined weight in binary blends (fly ash and Portland cement) and 20–30% in ternary blends (fly ash, Portland cement, and slag/amorphous silica). The associated requirements for fly ash properties are given in Table 5. Since both fineness and LOI vary continuously with boiler operation, AS 3582 requires that these two parameters be measured for every 500 t fly ash (or daily). The consistency of these parameters is the key in achieving predictable concrete performance. The standard deviation of measured results is therefore also an important indicator. Australia standard AS3972 and NZS3122 set out the requirement for fly ash used for Portland cement clinker in blended cement; the LOI limit is however not specified (ADAA, 2009c).

Table 5 Specified requirements for fly ash (to be used in normal class concrete) in the 2006 preliminary draft as a replacement for AS 3582.1-1998 (ADAA, 2009c)

Grade	Ultrafine	Fine	Medium	Coarse	Ref test method
Fineness, % passing 45 µm sieve	75	75	65	55	AS 3583.1
LOI, % maximum	4.0	4.0	5.0	6.0	AS 3583.3
Moisture, % maximum	1.0	1.0	1.0	1.0	AS 3583.2
SO ₃ , % maximum	3.0	3.0	3.0	3.0	AS 3583.8
Relative strength, % minimum	105*	–	–	–	AS 3583.6

* This means that the replacement of 50 kg of cement with 50 kg of fly ash will result in 5% increase in strength of the concrete produced

The present legislation more or less follows the international trends, notably those in Europe and the USA, and lack a firm scientific base. This is because the permitted empirical acceptance is too general to account for effects of fly ash properties on concrete quality. Some fly ashes that are suitable for use in cement/concrete may be excluded simply because certain properties are outside the permitted range.

Fly ash is still deemed as a waste under Australian legislation, regardless of any recycling process it may undergo. The 'waste' status puts fly ash at a disadvantage in the market place compared to natural materials because the latter are not subject to waste control for their utilisation even if they may have a greater environmental impact. Fly ash's 'waste' status also seems to conflict with sustainable initiatives in regulations of the same tier. For example, New South Wales is actively pursuing the reuse concept of coal combustion products, but fly ash is not listed as a reusable resource anywhere in its legislative documentation (Heeley, 2007). There seems to be understanding at both federal and state levels that the present legislation is inadequate to encourage beneficial utilisation of fly ash in Australia.

4.3.2 Canada

According to the Association of Canadian Industries Recycling Coal Ash (CIRCA), approximately 4.679 Mt of fly ash were produced in Canada in 2004 and 31% of the fly ash was used (CIRCA, 2004), almost all for cement manufacture and concrete/grout production. Canadian Standard Association (CSA) A3000 Cementitious Materials Compendium (2003 edition) covers specifications of cementitious materials such as fly ash for use in concrete, their chemical and physical test methods, and requirements for test equipment and materials. Chemical specifications for fly ash as per CSA A3001 are given in Table 6 (UNB, 2005).

In Canada, performance-based specifications of fly ash for use in concrete have been incorporated in the revised CSA standards in 2004 because the old prescriptive specifications excluded some usable fly ashes. The revised standards outline the roles that fly ash producers and contractors should play in ensuring satisfactory quality of produced concrete containing fly ash. As a result, the quantity of fly ash used has increased considerably. CSA also expanded its definition of fly ash to include those produced from co-combustion of coal and

petroleum coke, providing they meet the CSA A3001 specifications (Sherman, 2005). This alleviated pressure on demand for suitable fly ash in the Atlantic provinces of Canada where fly ash is used widely to accommodate abundant alkali-silica reactive aggregates in concrete production.

The federal government of Canada is actively promoting the utilisation of fly ash through a number of national initiatives on supplementary cementitious materials (SCM) (Sherman, 2005). The Action Plan 2000 on Climate Change initiative recognises the positive contribution of the use of SCM in cement/concrete to CO₂ emissions reduction and hence aims to lower barriers to their wider application. The LEED (Leadership in Energy and Environmental Design) Canada Rating System recognises buildings using SCM in their construction for their reduced environmental impacts. The revised CSA standards outline important considerations when large amounts of fly ash are used for LEED certificate. The federal government also encourages the use of SCM in all governmental construction projects and intends to use those projects as a national reference for the Canadian building industry. The *Best Practice Guide on the Use of SCM in Concrete Construction* has been published to aid successful utilisation of SCM in concrete (Sherman, 2005).

4.3.3 China

Intensive coal consumption in China has produced a vast quantity of coal fly ash; approximately 2.2 Gt of coal ashes (bottom ash also included) have been landfilled over the period 1949-2000, occupying about 300 km² of land (Barnes and Sear, 2004). A forecast sharp increase in the coal-based power generation in the next two decades suggests that coal ash produced may reach 570–610 Mt in 2020 (IEA, 2008c).

The Chinese government has pursued a policy of encouraging ash utilisation since 1950s to alleviate pressure on landfill disposal. For example, tax incentives are offered to projects involving coal ash utilisation. In 2000, the central government banned the use of solid clay bricks and tiles in new buildings in all municipalities, large coastal cities, and other regions where farm land is less than 0.053 hectares per capita (CEI, 2004). Consequently, 170 cities in China had phased out solid clay brick/tiles by 2004 (Chinanet, 2004). All these efforts have significantly boosted the fly ash utilisation. After rapid

Table 6 Chemical specifications of fly ashes for use in concrete in CSA A3001 'Cementitious Materials for Use in Concrete' (UNB, 2005)

Fly ash classes	Binary blended hydraulic cement						Ternary and quaternary blended cement
	N	F	CI	CH	S	SF	
SO ₃	3.0	3.0	3.0	3.0	3.0	3.0	3
Sulphide S	–	–	–	–	2.0	–	–
Insoluble residue	–	–	–	–	1.0	–	–
Loss on ignition	10.0	6.0	6.0	6.0	3.0	3.5	6.0

growth during 1990s, the ash utilisation rate reached 66% in 2002 (Sloss, 1999; Barnes and Sear, 2004). In more developed regions, such as Jiangsu province and Shanghai, nearly 100% utilisation has been reported (Cao and others, 2008). The construction industry is on course for strong growth with the central government's \$586 billion counter-recession stimulus package announced in November 2008. Prospects for ash utilisation are good in the years to come.

The national standard GB1956 regulates the property requirements, test methods and inspection rules for use of fly ash in cement/concrete production. When used as an admixture in concrete production (typically 50% Portland cement, 25% fly ash and 25% slag), fly ash is classified into three grades (*see* Table 7). The permitted maximum LOI are 5%, 8% and 15%, respectively. There are two grades of fly ash for use as additives in cement manufacture, for which the LOI needs to be no more than 5% and 8% respectively.

The lack of consistency in the quality of fly ash has become a major barrier to increased ash utilisation in China. This inconsistency results from the wide variation in the properties of coal burned. Virtually no steam coals other than those exported are washed in China and coal preparation plants are few. In some cases, non-optimised operation of old power plants also contributes to the variation in ash quality. Pretreatment of coal fly ash is therefore necessary for its utilisation in most regions of China.

4.3.4 European Union

According to the European Coal Combustion Products Association (ECOBA), 64 Mt of CCP were produced in its

15 member countries (EU15) in 2004; fly ash is the most important CCP with 68.2% of the total amount (Lewandowski and Feuerborn, 2008). Approximately 32% of the total fly ash was beneficially utilised in 2004: cement raw materials (5.7 Mt), constituent in blended cements (about 2.5 Mt), and concrete additions (about 5.9 Mt). Fly ash utilisation in cement/concrete over the period 1993-2004 is shown in Figure 11.

The harmonised European standard EN 450 is the most important standard for fly ash to be used in concrete production. EN 450 refers to siliceous fly ash only; calcareous fly ash derived from combustion of lignite cannot be used as concrete addition according to the standard. Calcareous fly ash is mostly used for backfilling of opencast mines (Feuerborn, 2005). The chemical and physical specifications in the latest standard EN 450-1:2005/A1:2007 are given in Table 8. There are also three categories of fly ash in the latest standard. Individual countries can decide which category of fly ash is accepted for the concrete production. Southern European countries, which are less prone to freezing temperatures in winter, may allow the use of fly ash with higher LOI values. In contrast, the central and northern European countries, where freezing temperatures are the norm in winter, may adhere to the stricter limits of 5% or 7% LOI (Kochert and others, 2009).

The latest EU 450 standard covers processed fly ashes that are produced by classification, sieving, re-drying, blending, grinding or carbon removal (Lewandowski and Feuerborn, 2008). This standard also permits the use of fly ash from co-combustion of biomass or waste. However, restrictions are imposed on the quantity of the biomass or waste: either should be no more than 20% by mass of the feedstock or with

Table 7 The properties requirements of fly ash for use as admixtures in concrete production or additives in cement manufacture (Wang and Cui, 2007)

Used as admixtures in concrete production			
	Grade		
	I	II	III
Fineness, % remaining on 45 µm sieve	<12	<20	<45
Ratio of water requirement	<95	<105	<115
LOI, %	<5	<8	<15
Moisture content, %	<1	<1	–
SO ₃ , %	<3	<3	–
Used as additives in cement manufacture			
	Grade		
	I	II	
Loss on ignition, %	<5	<8	
Moisture content, %	<1	<1	
SO ₃ , %	<3	<3	
The ratio of 28 days compressive strength, %	>75	>62	

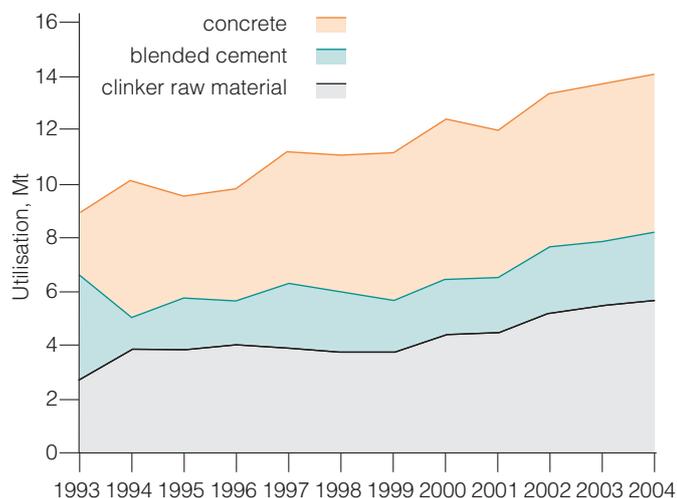


Figure 11 Fly ash utilisation in EU15 from 1993 to 2004, as a clinker raw material, a constituent of blended cements or as an addition for concrete production (Lewandowski and Feuerborn, 2008)

a maximum 10% by mass contribution to the resulting ash (Jones and others, 2006). These quantity limits ensure that the co-combustion fly ash will not have any properties differing significantly to coal-only fly ashes. In this regard, the following tests are required (Jones and others, 2006):

- Reactive silica >25%, routinely tested (1/month);
- Total oxides >70%. SiO_2 , Al_2O_3 and Fe_2O_3 have to be tested regularly again (1/month);

- Alkali content $\leq 5.0\%$, 1/month routine testing;
- magnesium oxide $\leq 4.0\%$, 1/month routine testing;
- Soluble phosphate ≤ 100 mg/kg, 1/month routine testing;
- The increase in the initial setting time ≤ 120 minutes, 1/month routine testing.

As is common to all CCP, fly ash utilisation in Europe is influenced by environmental legislation. Currently, the most important discussion revolves around the definition of CCP, or in general the definition of ‘by-product’ and ‘end of waste’. With the revision of the Waste Framework Directive 2008/98/EC, CCP are not confined by waste legislation and considered as ‘products’. They are however subject to the REACH (Registration, Authorisation, Evaluation and Restriction of Chemicals) regulations that came into force on 1 June 2007 (Feuerborn, 2009). Under REACH, all CCP including coal ashes manufactured in or imported into the EU have to be registered at the European Chemicals Agency. The registration requires information on the properties and the potential risks of the substances. Before this change to their legal status, CCP was in a seriously disadvantaged position in the marketplace compared to naturally occurring alternative materials (Sear, 2005). This was because CCP utilisation required waste exemption licensing from environmental authorities, which was a complex procedure creating man-made difficulties. The utilisation of fly ash may become more widespread in Europe as a result of its new legal status.

4.3.5 India

The utilisation of fly ash has increased significantly during

Table 8 Chemical and physical specifications for fly ash for use in concrete (Kochert and others, 2009)

Requirements	Limit	Limit description
Chemical analyses specifications		
Loss on Ignition (by mass)	Category A: <5% Category B: 2–7% Category C: 4–9%	Maximum LOI range
Free calcium oxide (by mass)	2.5%	Maximum value
Reactive calcium oxide (by mass)	10.0%	Maximum value
Reactive silicon dioxide (by mass)	25%	Minimum value
$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ (by mass)	Sum 70%	Minimum value
Alkali (by mass)	5.0%	Maximum value
Chloride (by mass)	0.10% (as Cl^-)	Maximum value
Soluble phosphate	100 mg/kg	Maximum value
Physical analyses specifications		
Fineness	Category N: 40% (by mass) retained on the sieve Category S: 12% (by mass) retained on the sieve	Maximum value on a 45 μm sieve
Activity index	75% at 28 days; 85% at 90 days	Minimum value
Density	± 200 kg/m ³	Maximum deviation from the producer-declared value
Soundness	10 mm	Maximum value

the period 1994–2002 due to the Fly Ash Mission initiated by the Department of Science and Technology, Government of India. The total amount of fly ash produced was estimated to be 130 Mt in 2007; fly ash that was utilised rose to 60 Mt (DST, 2008).

The increase in ash utilisation was attributed to the command/control directives from the government rather than to market forces. The most notable is the Fly Ash Utilisation Programme, which was renamed from the Fly Ash Mission in 2002. The Ministry of Environment and Forest (MOEF) has also issued notifications that comprise directives for the greater utilisation of fly ash (MOEF, 2008). For example, all coal or lignite based thermal power plants and their expansion units, which came into operation after 6 November 2008, are required to achieve 100% utilisation of fly ash generated within three years from the date of commissioning; those already in operation before 6 November 2008 are required to achieve 100% utilisation of fly ash within four years. The MOEF also restricted excavation of top soil for manufacture of bricks and requires the use of at least 25% of ash in bricks, blocks and tiles within a radius of 100 km from coal or lignite based thermal power plants. The Bureau of Indian Standardisation (BIS) has also taken several initiatives to encourage the utilisation of fly ash. For example, the BIS revised the IS 456 design code for plain and reinforced concrete to emphasise the use of fly ash in aggressive environment conditions.

According to the Building Materials & Technology Council of the Government of India (Jha and Prasad, 2009), half of utilised fly ash is used in cement/concrete production. The Indian standard IS 3812 specifies two grades of fly ash for use as pozzolan or admixture, respectively. Table 9 compares both the chemical and physical requirements in British, American and Indian standards. With regard to LOI, the requirement seems more stringent in India than in the other two countries.

Most of the Indian power plants are equipped with wet systems for collection of fly ash, because they are cheaper than any other modes. However, the wet collection reduces the pozzolanic reactivity of the fly ash. As dry facilities, such as ESPs and baghouses, are increasingly installed, more dry fly ash will become available. Furthermore, it will be necessary to develop a wider range of fly ash products by the means of beneficiation, classification and upgrading to increase high value-added fly ash utilisation.

4.3.6 Japan

The fly ash utilisation rate has steadily increased from 1994 to 2004 and a marked reduction in landfilled fly ash has been seen since 1999. Fly ash production amounted to 10.85 Mt in 2004, and the utilisation rate reached 90% in 2004, up from

Table 9 The specifications of fly ash for use in cement/concrete in the UK, the USA and India (Jha and Prasad, 2009)						
Requirement	EU Standard EN 450	American Standard ASTM C618	India Standard 3812 (Part I)*		India Standard 3812 (Part II)†	
			SPFA‡	CPFA§	SPFA	CPFA
Chemical analyses specifications						
Loss on Ignition (maximum)	Category A: <5% Category B: 2–7% Category C: 4–9%	6.0%	5%	5%	5%	5%
CaO (maximum)	10%	–	–	–	–	–
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ (min.)	70%	70% (Class F);				
50.0% (Class C)	70%	50%	70%	50%		
Alkali as Na ₂ O (maximum)	5%	1.5%	1.5%	1.5%	1.5%	1.5%
Chloride (maximum)	0.10%	–	0.05%	0.05%	0.05%	0.05%
Physical analyses specifications						
Fineness (maximum mass percentage retained on 45 µm sieve)	Category N: 40%; Category S: 12%	34%	34% (optional)		50% (optional)	
* India Standard 3812 (Part I): for use as pozzolan in cement, cement mortar and concrete						
† India Standard 3812 (Part II): for use as admixture in cement, cement mortar and concrete						
‡ SPFA: silicious pulverised fuel ash						
§ CPFA: calcareous pulverised fuel ash						

80% in 1999. The utilisation rate was projected to remain at this level or slightly higher after 2004 (Ishikawa, 2007).

The amount of coal ash produced from electric utilities is approximately three times that produced from general industries (Yamazaki and others, 2005). Most power plants in electric utilities use pulverised coal fired boilers, with only three units employing Pressurised Fluidised Bed Combustion (PFBC) technology (Yamazaki and others, 2005). All the power plants use imported coals, except the Sunagawa and Naie power plants in the northeastern island of Hokkaido. In the general industries, approximately 60% of plants are pulverised coal fired, 20% employ the fluidised bed technologies, and the remaining 20% are stoker fired.

In Japan, the major use of fly ash is as a substitute for clay in cement manufacture. For example, in 2003, 70% of the fly ash was used as cement raw material and only 5% as cement/concrete admixture (Yamazaki and others, 2005). However, Japan's cement output has ceased increasing or even started to decrease in recent years. The expansion of ash use in the cement industry will therefore be unlikely to continue. To increase fly ash utilisation further, the Centre for Coal Utilisation Japan formulated a new strategy for the 21st century, with a focus on concrete admixtures, artificial aggregates in civil engineering applications, and other potential options involving use of large quantities of fly ash. Since all these applications currently account for small shares of the total fly ash utilisation, there should be substantial room for expansion. The Japanese Industrial Standard (JIS) A 6201 provides specifications of fly ash for use in concrete (see Table 10). Four grades of fly ash are more carefully defined to provide increased choices for users. The LOI requirement is relatively more stringent than that in other countries.

There are stringent three-level quality controls for fly ash produced in thermal power plants in Japan. The recovery quality control determines whether the fly ash recovered meets the specification of relevant regulatory standards. The manufacturing quality control requires quality testing before and after fly ash is processed through classification, blending and other treatments. When fly ash is delivered by trucks or marine vessels to the users, a test report on the fly ash quality is required to be enclosed with the freight.

4.3.7 Russia

The coal industry in Russia has undergone drastic changes during the past two decades. Coal consumption dropped sharply by 42% from 182 Mt in 1990 to 106 Mt in 2002 (see Table 11). Since the restructuring of the power generation industry since 2003, coal consumption has steadily recovered and reached 132.8–145.6 Mt in 2005 (Putilov and Putilova, 2005). Switching from gas-fired to coal-fired power generation remains economically attractive in Russia, which is projected to further increase coal demand by more than 50% from 2006 through to 2030 (IEA, 2008d).

Similarly (compared with the patterns of coal consumption), the ash generation dropped sharply from 1990 to 2002 and then recovered from 2003. However, the ash utilisation rate showed a general trend of increase from 9.4% in 1990 to some 19.6–21.5% in 2005; the absolute quantity of ash utilised in 2005 has recovered to the 1990 level. The ash utilisation rate in Russia is much lower than that in other countries.

The state standard GOST 25818 sets out specifications of fly ash for use in concrete. Table 12 compares the permitted limits on key properties of fly ash between GOST 25818 and EU standard EN 450. The permitted limits vary considerably for different types of fly ashes and their parent coals, whereas those limits have been largely harmonised and are generally more strict in Europe. The permitted maximum LOI values are much higher for hard coal and anthracite in the Russian standard.

One of the major barriers to increasing ash utilisation in Russia is the lack of awareness of its benefits in power companies (Putilov and others, 2007). For example, Russian power companies are reluctant to install dry ash handling facilities or exploit options for ash utilisation. More than 80% of fly ash produced in Russian thermal power plants is currently disposed of in lagoons as low concentration slurry (Putilov and Putilova, 2005). The wet disposal of ash not only poses a contamination threat to the environment, but also degrades the quality of fly ash required for certain applications. Another major barrier is the weak federal-level legislation on promoting the beneficial utilisation of coal fly ash (Putilov and others, 2007).

Table 10 The specifications in JIS A 6201 for fly ash utilisation in concrete (Ishikawa, 2007)

Requirement		Type I	Type II	Type III	Type IV
Loss on Ignition, wt%, maximum		3.0	5.0	8.0	5.0
Fineness	% remaining on 45 µm sieve, maximum	10	40	40	70
	Specific surface area, cm ² /g, minimum	5000	2500	2500	1500
Activity Index . %, min	at 28 days	90	80	80	60
	at 91 days	100	90	90	70
Silicon dioxide, wt%, minimum		45.0			
Density, g/cm ³ , minimum		1.95			

Table 11 The annual ash generation, utilisation and disposal over the period 1990-2005 (Putilov and Putilova, 2005)

Year	1990	1995	2000	2002	2005
Coal consumption, Mt/y	6				
Average ash content, wt%	27.5	26.3	20.8	21.4	21.0
Ash generation	50.0	33.7	25.0	22.7	27.9–30.6
Ash utilisation without station service, Mt/y	4.5	1.9	3.1	3.3	4.5–5.6
Ash disposal, Mt/y	43.0	30.1	20.7	18.3	22.4–24.0
Ash utilisation rate, %	9.0	5.6	12.4	14.5	14.7–20.1

Table 12 Comparison of permitted limits on key properties of fly ash between Russian and EU standards (Putilov and Putilova, 2005)

Parameter	Coal type	Permitted limits (wt%) as per GOST 25818				Permitted limits (wt%) as per EN 450
		I	II	III	IV	
Loss on ignition, wt%						
acid ash	anthracite	<20	<25	<10	<10	Category A <5
	hard coal	<10	<15	<7	<5	Category B <2–7
	brown coal	<3	<5	<5	<2	
basic ash	brown coal	<3	<5	<3	<3	Category C <4–9
Reactive CaO content						
acid ash	any	<10				<10
basic ash	brown coal					
Free CaO content						
acid ash including free CaO	any	not normalised				<2.5
basic ash including free CaO	brown coal	<5	<5	N/D	<2	
SO₃ content						
acid ash	any	<3	<5	<3	<3	<3
basic ash	brown coal	<5	<5	<6	<3	
MgO content	any	<5	<5	N/D	<5	<4
Fineness R₈₀, wt% remaining on 80 µm sieve						R ₄₅ , wt%
acid ash	any	<20	<30	<20	<15	Category N <40 with ±10% variation
basic ash	brown coal	<20	<20	<30	<15	Category S <12
Chloride content, wt%	any	N/D				<0.1

4.3.8 South Africa

Fly ash production increased with the number of large PCC power plants that came on-line in the 1980s. Coal fired in domestic power plants generally has a high ash content, in the range of 30–35% (Couch, 2006). Fly ash produced from coal-fired power generation was estimated to be 35–41 Mt in 2006. Ash utilisation rose to almost 2 Mt in 2005 from just 20 kt/y in the 1980s (Kruger and Krueger, 2005).

Such a low utilisation rate of fly ash is due primarily to the fact that power stations are generally located at significant distances (>300 miles) from industrial zones or economic hubs where the electricity demands are high (Kruger and Krueger, 2005). This particular geographical distribution of ash sources means that the cost of ash transportation is high, which in many cases reduces the interest in ash utilisation. Being located far from population-dense regions, coal-fired power plants naturally exploit the easy availability of empty land that can be used to landfill the ash produced. To make

ash utilisation economically attractive, coal ash has to be converted to products with high added-value. To this end, an intensive national R&D programme was committed to support both fundamental and applied research into the potential utilisation options for fly ash over the period 1980-87 (Kruger and Krueger, 2005).

Fly ash utilisation is dominated by its use in cement/concrete production, particularly with the sharp increase in demand for cement due to the economic boom of the 1980s. Fly ash for use as cement extenders together with ordinary Portland cement has to comply with the specification in the South African Standard SABS 1491-Part II. The standard SABS EN 197-1 specifies fly ash used to make blend cements. Both standards limit the maximum LOI to 5% by mass. According to SABS 1491-Part II, the ash fineness has to satisfy that no more than 12.5% of the ash particles remain on a 45 µm sieve (Kearsley and Wainwright, 2003).

However, the market size of ash utilisation in cement/concrete is constrained for the following reasons. The total capacity of cement clinker production in South Africa is only about 10 Mt/y, far less than the total fly ash production. Furthermore, only about 30% of the cement may be substituted by fly ash in order to produce concrete of acceptable quality. The logistics and transport costs further limit the market size. Some large-volume applications such as ash mine backfill and road base materials are, however, of low value. To further increase high-value utilisation of fly ash, some specialty fly ash products have been developed in South Africa. The ash marketer Ash Resources, for example, uses beneficiation and other processing technologies to produce four construction products: Dura-Pozz®, Super-Pozz®, Pozz-Fill®, Pozz-Sand®.

4.3.9 USA

The US government's attitude toward CCP is very positive. In 1993 and 2000, the Environmental Protection Agency (US EPA) preliminarily determined that no environmental harm was identified with the beneficial use of CCP and that these materials did not warrant regulation as a hazardous waste. However, the US EPA recognises that unencapsulated uses of CCP, such as underground mine backfills and in agricultural applications, require proper hydrogeologic evaluation to ensure groundwater protection. The US EPA has continued to look at the toxic nature of solid wastes from power plants. A new rule is expected from the US EPA in the near future.

Fly ash is the largest CCP stream in the USA; approximately 41.6% of the total fly ash produced (72.5 Mt) was utilised beneficially in 2008 (ACAA, 2009c). Use in cement/concrete accounted for 52.35% of the total ash utilisation in 2008. The usage rates of fly ash in cement and concrete/grout over the period 2001-08 are shown respectively in Figure 12. It can be seen that fly ash is used predominantly in concrete/grout production and that use in cement follows a broad trend of increase. Use of fly ash in other applications such as structural fills, embankments, and soil stabilisation, has also combined to account for nearly half of total fly ash utilisation. The US Department of Energy (US DOE) and the

US Environmental Protection Agency (US EPA) set goals to increase the utilisation of CCP (44.5% in 2008) to 50% by 2011 (Buckley and Pflughoeft-Hassett, 2007). To achieve this goal, both agencies have created or been supporting programmes that encourage CCP use. Such programmes include the Coal Combustion Products Partnership (C²P²), Recycles Materials Research Centre, Green Building Council Leadership in Energy and Environmental Design (LEED®) programme (Buckley and Pflughoeft-Hassett, 2007). A newly formed programme, the Industrial Resources Council, was created with the aim of bringing together industry associations of different wastes or by-products to achieve similar goals.

Coal fly ashes are required to meet specifications in the ASTM C618 standard for use in concrete. ASTM C618 classified two types of fly ash: Class C and F. Class C fly ashes are rich in lime, containing typically 10–40% (by mass) CaO; Class F fly ashes are highly siliceous with a CaO content of less than 10%. Consequently, class C fly ashes take part in both cementitious and pozzolanic reactions, whereas class F fly ash is predominantly involved in pozzolanic reactions during the hydration process (Naik and others, 2003b). Class F fly ashes are thus often preferred to mitigate the effect of alkali silicate reactions (ASR) in concrete. Specifications for class C and F fly ashes are given in Table 13. The major difference between the class C and F fly ash is the minimum requirement for the total mass proportion of silica, alumina and hematite. The permitted maximum LOI values required for class C and F fly ash are the same, but for the class F fly ash the permitted limits may be relaxed if either acceptable performance records or laboratory tests are made available.

Table 13 also includes the specifications in the M295 standard for coal fly ash for use in concrete in transportation projects,

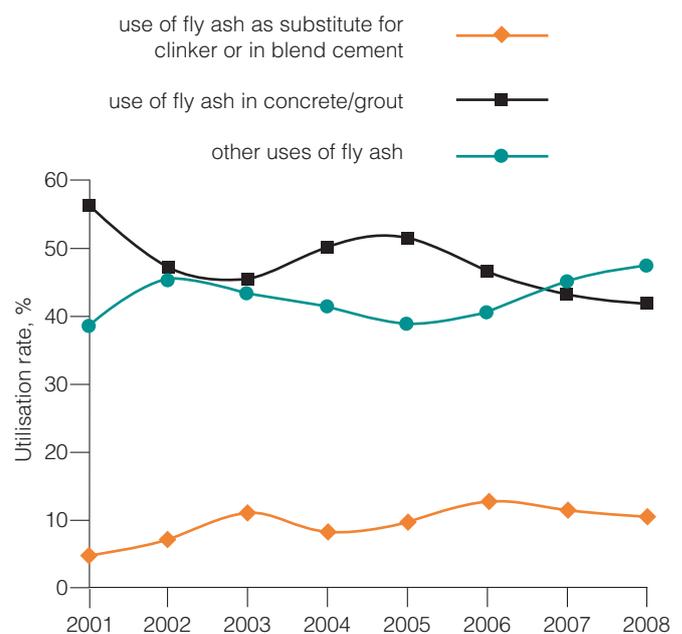


Figure 12 The utilisation rate of fly ash for use in cement and concrete/grout in 2001-08 (ACCA, 2009c)

Table 13 Specifications for fly ash that is used in concrete in ASTM C618 (Dockter and Eylands, 2003) and AASHTO M295 (Boral Material Technologies, 2009)

Requirement	ASTM C618, Class F/C	AASHTO M295, Class F/C
Loss on Ignition, wt%, max	6.0*	5.0
Mass percentage retained on No 325 mesh sieve, pore size 45 µm, max	34	34
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , wt%, min	70.0/50.0	70.0/50.0

* For class F fly ash, normally 6% max. but 12% max. may be approved by user if either the acceptable performance records or laboratory tests are available

which is regulated by the American Association of State Highway and Transportation Officials (AASHTO). The specifications are similar to those in the ASTM C618 except for the stricter LOI requirement. This reflects the greater demand for concrete that has a higher resistance to freeze-thaw cycles in many constructions for transportation.

In recent years, a wave of safety concerns over disposal of fly ash has swept across the USA, culminating in the largest fly ash spill in US history that occurred at the Kingston Fossil Plant in Tennessee in December 2008. This incident prompted the US EPA to immediately review coal ash disposal sites across the USA and a bill was proposed for the regulation of coal ash disposal impoundments with safe design and regular inspections. The result was an increase in the cost of ash disposal and the complexity of licensing, making utilisation of fly ash more attractive to boiler operators. On the other hand, the public perception of fly ash and CCP in general suffered after these incidents. If the general public becomes reluctant to accept concrete products containing fly ash, this may reduce the prospects for further increases in fly ash utilisation.

The 2009 American Clean Energy and Security Act, although only approved by the Lower House of Congress, shows for the first time that the USA is committed to reducing its greenhouse gases emissions. The bill aims to cut emissions by 17% from the level in 2005 by 2020, then by 83% by 2050. Given the role of fly ash use in cement/concrete in curbing CO₂ emission, the act thus creates incentives for the US cement and construction industries to exploit increased use and new applications of coal fly ash and other types of CCP. Furthermore, the act also indicates that boiler operators will likely be mandated to reduce their CO₂ emissions. Beneficial use of some of the fly ash they produce may well be one of the potential measures for them to meet their obligations to reduce CO₂ emissions.

4.4 Summary and discussion

This chapter discusses the benefits of using fly ash in cement/concrete production and the impacts of excessive carbon-in-ash. It is clear that the absolute quantity of unburnt carbon alone is not sufficient to judge the suitability of a fly ash for use in cement/concrete production. To precisely determine that suitability, the actual morphological properties of fly ash need to be taken in to account. However, at present only a few national regulatory standards, for example those in

the USA, involve terms for performance-based specifications for fly ash that is used in concrete production. Nevertheless, it does not mean the quantity-based LOI specifications are dispensable. LOI is still an important indicative parameter even just from the perspective of fuel-saving. As it can be quickly measured, LOI still serves practically as the first step in fly ash quality control for use in cement/concrete.

The permitted maximum range of LOI for fly ash that is used in concrete production as substitute for ordinary Portland cement in major coal-consuming countries is also reviewed, and summarised in Table 14. Apart from China and Russia where high LOI levels are allowed for certain fly ash, other countries require similar LOI limits for fly ash for use in concrete.

Table 14 Summary of requirements for LOI in different major coal-using countries

Countries	LOI limits, %, maximum
Australia	3–6
Canada	3–10
China	5–15
EU	Type A: 5 Type B: 2–7 Type C: 4–9
India	5
Japan	3–8
Russia	Basic ash: 3–5 Acid ash: 2–25
South Africa	5
USA	Class F: 6 (12) Class C: 6

5 Removal of carbon-in-ash

Chapter 2 reviewed measures for the prevention of excessive carbon-in-ash in PCC power plants. This chapter discusses how to reduce the unburnt carbon content of run-of-station fly ash. Ash beneficiation can remove some impurities such as ferromagnetic materials and improve the homogeneity of ash particles. In conjunction with fly ash blending, beneficiation can produce various grades of ash products with consistent qualities for different applications. The resulting diversity in ash products increases the revenue from ash sales for ash producers/marketers. There is a consensus among fly ash producers, representatives of ash trade organisations, and end users that the key to turning ash into a valuable resource lies in ash beneficiation (Barnes and Sear, 2004).

5.1 Classification

Mechanical classification is probably the most widely used practice to remove coarse particles from finer ones, and thus obtain different size fractions. Since the unburnt carbon generally concentrates in large ash particles, classification is useful in reducing the carbon content of fly ash. The efficacy of this method is dependent on the degree to which the carbon-rich particles are discretely distributed as well as their sizes and shapes. Dry classification generally becomes uneconomic for particles smaller than $45\ \mu\text{m}$ (325 screen mesh size). Since fly ash typically has more than half of particles finer than $45\ \mu\text{m}$, classification is usually employed as part of a sophisticated beneficiation process to pre-separate the raw fly ash into various size fractions, which increases the overall efficiency and consistency of the whole process. One successful example of using mechanical classification is the Maasvlakte Fly Ash Processing Plant located in Rotterdam in the Netherlands, which has been operated by Vliegassie since 1995. With a capacity of 250,000 t/y, this plant has an important role in maintaining the Netherlands' record of using

100% of its coal fly ash through consistently meeting the users' requirements for fly ash. This fully computer-controlled plant is used for both storage and upgrading of fly ash from the adjacent Maasvlakte Power Plant, which consists of an intake silo (capacity of 9000 t), an upgrading plant and an end-product silo (capacity of 32,000 t). The upgrading plant incorporates mechanical sieving mechanisms whereby the carbon content can be reduced to less than 5% and the end product can be improved to over 70% finer than $45\ \mu\text{m}$ (Vliegassie, 2009).

In addition, pneumatic classification systems are also commonly used in commercial fly ash process facilities. One of the problems with mechanical sieving is the flocculation clogging the sieve apertures due to the high fineness of ash particles. Pneumatic classification is dependent upon not only size differences but also the specific gravities and shapes of individual particles. Based on the settling rate of ash particles in air, pneumatic classification can effectively separate out particles down to $10\ \mu\text{m}$ with a fairly large throughput. This type of system is used intensively in the ash process facilities of Ash Resources in South Africa to produce their flagship products: Dura-Pozz® and Super-Pozz®.

Pneumatic classification systems typically take the form of cyclone classifiers whereby centrifugal forces push the coarse particles toward the inner wall to separate them from finer particles. One undesirable consequence of such centrifugal separation is that large carbon particles may be crushed into smaller fines when being forced to collide against the inner cyclone wall or with other large ash particles. Some carbon-containing fines will be carried away and so the separation efficiency suffers. One way to alleviate this problem is to place several cyclones in tandem so that centrifugal separation can take place in several stages, resulting in higher separation efficiency and sometimes reduced crushing of large particles

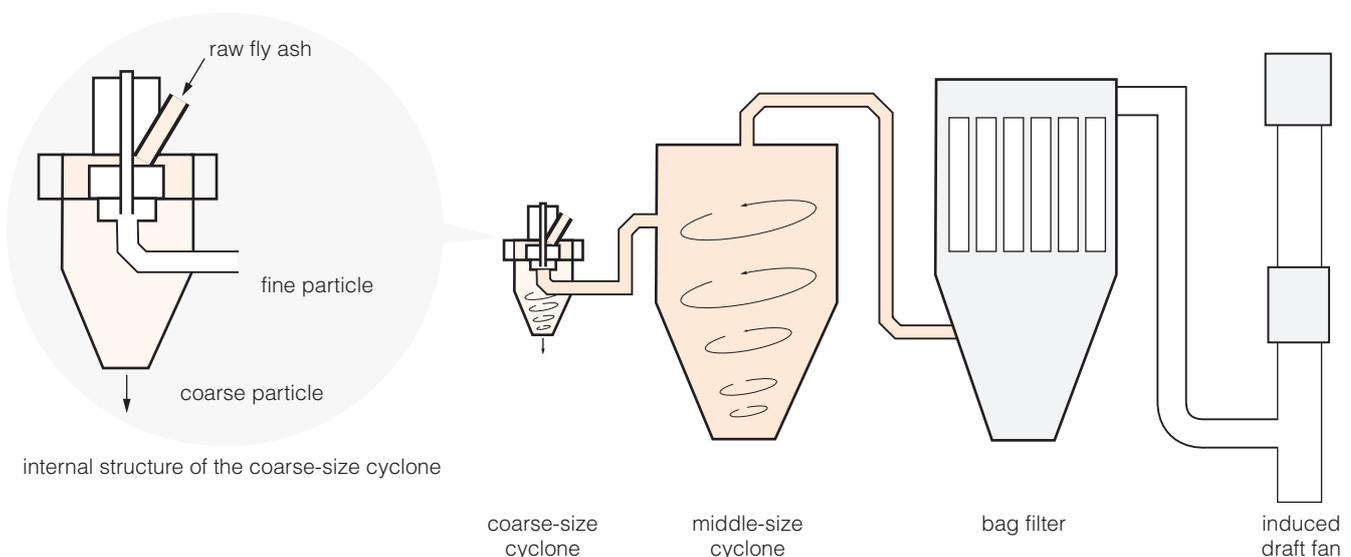


Figure 13 The multi-stage air classifier (Park and others, 2003)

(Park and others, 2003; Groppo and others, 2009). For example, a multi-stage pneumatic classification system has been devised in South Korea to tackle the high carbon-in-ash problem associated with burning domestic anthracite coals (Park and others, 2003). Figure 13 shows the schematic diagram of this multi-stage system which comprises a coarse-separation cyclone, a middle-size-separation cyclone, a bag filter to capture very fine particles and an induced draft fan. Results from the pilot-scale trials of such a system commissioned by Geocom Material Inc show that the LOI can be reduced effectively from 8.4% to 2.9% with 73% yield rate of refined ash product (Park and others, 2003). There were plans to build a full-scale multi-stage system at the 2×200 MWe Seocheon power station in 2003 to resolve the excessive carbon-in-ash problem that occurred after low NO_x arch-firing equipment had been retrofitted to the plant (Park and others, 2003). More recently, the University of Kentucky in the USA and the Fisher-Klosterman Incorporation jointly investigated a similar integrated pneumatic classification system (the Buell Model C 18-9) which consists of two cyclone-based separation units and a fabric filter (Groppo and others, 2009). They found that such a system was capable of making a 200-mesh split of the feed fly ash and producing a finer ash (85.2% yield rate) with LOI lower than 3%. However, the multi-stage pneumatic classification system did not prove successful for fly ash from coal blends (Smith, 2005).

The propensity of break-up of large particles into fines is nevertheless still the inherent flaw of pneumatic classification systems. If the unburnt carbon present in fly ash concentrates in fine particles, pneumatic classification is not an effective method for carbon reduction. This is because carbon particles would actually be retained within the inner vortex generated in the cyclone due to their lower densities compared to those of ash particles of similar fineness. This explains why the product ash from pneumatic classification generally has a somewhat higher LOI value compared to that produced by other carbon reduction technologies described in the rest of this chapter.

5.2 Froth flotation

Froth flotation exploits the hydrophobicity of unburnt carbon in fly ash. In a typical froth flotation process (see Figure 14), air bubbles produced in an agitated tank effectively collect the unburnt carbon particles and transport them to the top of the tank where they are retained in a stable froth. The unburnt carbon particles can be recovered from the froth at regular intervals; what remains in the tank is essentially a low-carbon pozzolanic slurry, which is subsequently thickened, filtered and dried to produce saleable ash products. A high agitation speed has been reported to favour the froth flotation performance (Walker and Wheelock, 2006).

However, unburnt carbon particles that have been oxidised intensively are difficult to float due to their reduced hydrophobicity (Walker and Wheelock, 2006). Flotation collectors can be used to render them more hydrophobic; oily collectors, such as kerosene, fuel oil and other petroleum distillates, are the most widely used. However, generally large

quantities of such collectors are required to achieve the desired carbon recovery rate. Intensive research efforts have therefore been made to develop high efficiency collectors. A collector composed of petroleum sulphonate and fuel oil (1:10) was patented by Groppo and Brooks (Walker and Wheelock, 2006). A good carbon recovery rate can be achieved with just 2.8 kg of this mixture collector per tonne of fly ash. Two collector mixtures, 4-dodecylphenol (DDP)/hexadecane (HEX) and nonylphenol (NP)/HEX, were developed at the Pennsylvania State University in the USA (Harris and Wheelock, 2008). The NP/HEX mixture was found to be more effective than the DDP/HEX mixture, particularly for oxidised carbons, although the tailing (remaining slurry in the flotation tank) yield dropped significantly. Although using a larger dosage of flotation collector generally yields a higher carbon recovery rate, this recovery rate appears to level off beyond a certain dosage limit. It is therefore important to determine carefully the minimum collector dosage to control the cost. The carbon recovery rate is also found to be affected by the composition of a mixture collector. As an example, in NP/HEX the NP is normally more expensive than HEX. An optimum composition needs to be defined to minimise the cost.

It has been found that some reagents, such as methyl isobutyl carbinol (MIBC) and pine oil, can considerably reduce the collector dosage required to achieve a desirable carbon recovery without any adverse effects. These reagents are called frothers; they allow flotation collectors to selectively adsorb onto carbon particles. For example, to meet the ASTM specification of 6% LOI, only a small dosage (0.10 cm³/100 g fly ash or less) of the NP/HEX (1:1) collector was required when MIBC with a dosage of 0.05 cm³/100 g fly ash was

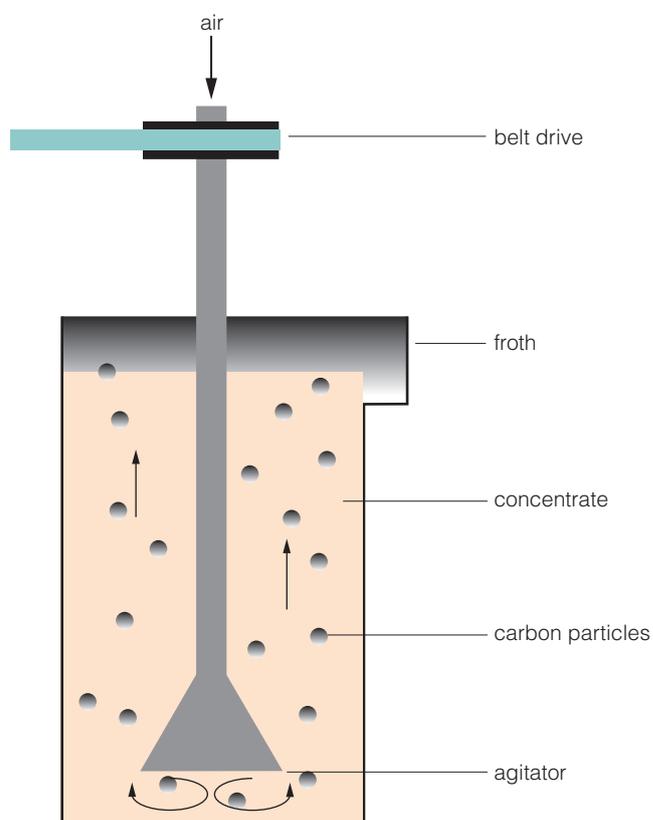


Figure 14 A froth flotation tank

used (Drzymala and others, 2005). A mild increase in the dosage of NP/HEX collector to 0.4 cm³/100g fly ash, with the MIBC dosage kept the same, was sufficient to achieve a nearly 99% carbon recovery rate as well as <0.73% carbon content of the tailing ash (Walker and Wheelock, 2006). As an alternative to frother, ultrasonic energy can be used to emulsify flotation collectors in order to reduce the collector dosages (Minkara and Heavilon, 1999). However, such a method is not as efficient as addition of frother to the flotation slurry.

Froth flotation can be used to recover fly ash that has been disposed of in lagoons or landfills. Old fly ash storage sites can thus be reclaimed so that construction of new disposal sites can be avoided or postponed. The buried fly ash that has not had the opportunity to be processed can be turned from wastes into high quality saleable ash products. Since dry fly ash is not required for froth flotation processing, the ash producers do not need to alter their conventional ash handling practices. In contrast to dry ash processing, froth flotation can be conducted nearby ash disposal sites. This releases the pressure on operators to find available space on the plant site to install dry ash handling facilities (Tyra and others, 2003). Fly ash processing is thus decoupled from ash production, which offers great flexibility to plant operators as they can adjust their fly ash processing capacity against the demand. For example, in regions where cold weather is the norm, ash production peaks while construction activities are weak. Demand for fly ash for use in concrete is therefore low. The plant operators can deposit the excessive fly ash and recover it later during warmer periods when the demand picks up.

In the USA, there has been interest in recovering the unburnt carbon from disposed ash as a fuel source over the past decade. An integrated Fuel-Float™ process has been jointly developed by the University of Kentucky Center for Applied Energy Research, the US DOE and the Western Kentucky Energy. Froth flotation is an important component of this process, as well as the hydraulic classification and the gravity (spiral) concentrating process. A carbonaceous fuel with a calorific value of 15,119 kJ/kg has been recovered in a pilot-scale trial (Groppo and Robl, 2001). This fuel showed acceptable reactivity probably due to its relatively high porosity. It was claimed that a higher grade carbonaceous fuel may be produced by using column flotation or other cleaner flotation methods. Froth flotation has also found its application in carbon recovery of bottom ash. For example, at the Tuncbilek thermal power plant in Turkey, the process increased the calorific value of unprocessed bottom ash from 491 kJ/kg to 1348 kJ/kg of the recovered carbon-rich product (Yamik and Dogruoz, 2008).

In addition, very fine fly ash ($\leq 5 \mu\text{m}$ in normal diameter) can be recovered from disposed ash using froth flotation for use as polymer filler and a super pozzolanic concrete additive. In a project conducted by the University of Kentucky Center for Applied Energy Research, the recovery yield reached 21%; the recovered ash product contained as high as 64% of such very fine fly ash ($\leq 5 \mu\text{m}$) (Robl and others, 2008).

Froth flotation is a key component of the fly ash beneficiation process developed by Rock Tron Limited in the UK. This

process is designed to turn 100% of the run-of-station, stockpiled or landfilled fly ash into a variety of value-added ash products and a solid carbonaceous fuel (Smith, 2005). Successful pilot-scale trials were completed on fly ashes from the Aberthaw Power Station in South Wales and the from Fiddler's Ferry Power Station in Cheshire during the 1990s. Subsequently, after a successful demonstration project funded by Scottish & Southern Energy, Rock Tron commissioned a full-scale commercial plant at the Fiddler's Ferry station in February 2009 (RockTron, 2009).

5.3 Triboelectrostatic separation

Triboelectrostatic separation exploits the difference in electron affinity between mineral ash particles and carbon particles. When an electric field is imposed, carbon particles lose electrons and become positively charged due to their lower electron affinity, while the mineral ash particles gain electrons and become negatively charged. This charging spreads to all the particles as they collide with each other (so called triboelectrostatic effect). Separation occurs when these charged particles are diverted to electrodes of the opposite charge. There are a number of triboelectrostatic separators on the market with the major difference lying in the various mechanical designs for physical collection of the two separated particle streams.

Separation Technologies LLC in the USA, now a subsidiary of Titan Cement Company, was the first and most important company to supply triboelectrostatic separators to the fly ash separation market. Its triboelectrostatic separator is of a typical design as shown in Figure 15. Fly ash is fed from a silo through a vibrating screen and then distributed evenly into a thin gas (6.35–19 mm) between two parallel plane electrodes where separation takes place. A high-speed moving open-mesh belt conveys the separated particles in opposite directions. The carbon and the mineral particles are collected at each end of the belt, respectively. Separation Technologies' (ST) triboelectrostatic separator is compact (typically 10 m long, 1.5 m wide and nearly 3 m high) and requires a low capital investment and a relatively small space at the power plant site (Smith, 2005). The spread length of the conveyor belt is typically 6 m, but can vary with the processing capacity or the space available on the site. It can process up to 36 t of fly ash per hour. Its operational power consumption is low, about 1–2 kWh for each processed tonne of fly ash (Barnes and Sear, 2004). There are 18 installations in operation or under construction at eleven power stations throughout the USA, Canada, the UK and Poland (Separation Technologies, 2009b).

The ST triboelectrostatic separator can turn fly ash into two branded products: ProAsh® and EcoTherm™. ProAsh® is the carbon-lean fraction after the separation, which meets the standard specification for use in concrete/grout production. A wide variety of fly ashes with LOI up to 30% can be processed in the ST triboelectrostatic separator. The produced ProAsh® has a consistent LOI of about 2%, well below the permitted maximum LOI limits in almost all the main national standards. ProAsh® is a sustainable building product that can contribute to LEED certified building projects.

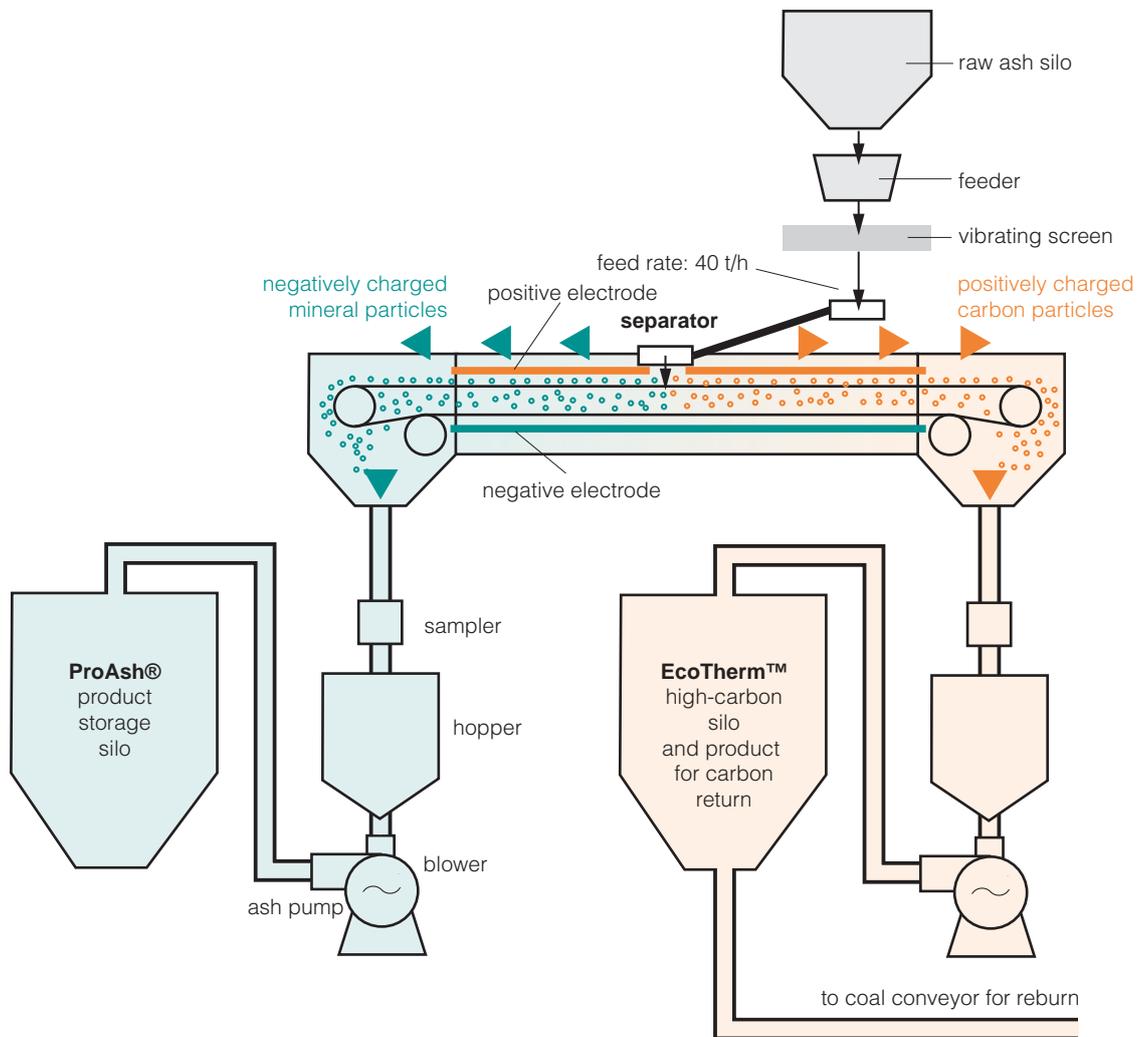


Figure 15 The STI triboelectrostatic separator (Separation Technologies, 2009a)

EcoTherm™ is the carbon-concentrated fraction that can serve as a solid fuel with consistent quality.

The ST separator has helped many utilities and ash marketers to address their excessive carbon-in-ash issues. For example, the Florida-based St John's River Power Park faced a high carbon-in-ash (LOI of 15–28%) problem as a consequence of co-combustion of up to 20% of petroleum coke (Smith, 2005). The LOI can be effectively reduced to a consistent level of less than 3.5% using a ST triboelectrostatic separator. A series of durability tests have demonstrated the suitability of the processed low-carbon ash for use in transportation construction projects. The Longannet power plant in Scotland also saw the unburnt carbon level of its fly ash rise from 3% to 7–10% or even 15% with less efficient combustion after retrofit of low NO_x burners (Smith, 2005). An ST separator has been put in place to process the fly ash. The processed ash had a low LOI of about 5% and was sold to the Dunbar cement plant for partial replacement of cement clinker. It was reported that the Scottish Environmental Protection Agency has permitted combustion trials of the carbon-concentrated fraction that were intended to feed back to the power plant. Throughout Virginia, North Carolina and South Carolina in the USA, the intensive use of reactive aggregates and poor availability of low alkali cement makes

coal fly ash a highly desirable additive in order to mitigate the prevailing alkali-silicate reaction problem. The ST triboelectrostatic separation process enables the Roxboro plant in North Carolina to produce a fly ash product under the brand ProAsh® that is in high demand by the ready-mixed concrete producers in these regions. The quality consistency of the processed ash also allows for standardised mix designs with no need to frequently adjust the ratio of air-entraining admixtures.

With respect to utilisation of the carbon-enriched fraction from a ST separator, returning it back to the boiler for reburning is a common practice, which can reduce the total fuel cost. The first reburning trial on the carbon-enriched fraction was conducted at the New England Power and Salem Harbor power plant in the USA in 1995 (Bittner and Gasiorowski, 2005). The trial proved that directly re-injecting the carbon-enriched fuel is a viable reburning method; the energy recovery from this fuel was similar to that from coal (>85%). Flame shape and stability were unaffected; air emissions and the stack opacity were found to remain acceptable (Bittner and Gasiorowski, 2005). In addition to direct injection into the furnace, the carbon-enriched fuel can also be added to the coal prior to the coal pulverisers. A full-scale trial of such a method was made by the Maryland-based

Baltimore Gas and Electric in the USA (Bittner and Gasiorowski, 2005). The energy recovery was also found to be similar to that from coal; the precipitator performance and particle/gas emissions were not significantly affected. Based on results from both trials, Separation Technologies LLC concluded that the co-grinding addition method is preferable to the direct injection method (Bittner and Gasiorowski, 2005). The company subsequently constructed carbon-reburning systems based on the co-grinding addition method at the R D Morrow power plant of the Southern Mississippi Electric Power Association and the Belledune plants of Energie NB Power in Canada (Bittner and Gasiorowski, 2005). Reburning rates of 20–33 t/h have been achieved with no adverse effects observed on the combustion performance, air emissions and the electrostatic precipitator performance. Such reburning systems are now in routine operation at the two plants.

The Center for Applied Energy Research of the University of Kentucky developed a different design of the triboelectrostatic separator based on pneumatic transportation of the fly ash. The schematic diagram of this design is shown in Figure 16. It comprises a pneumatic feeder, a high voltage separation chamber, and a vacuum-induced sample extraction unit. Fly ash is carried by compressive air through a tribocharging pipe whereby the ash particles take on electrical charges. The charged ash particles flow into the separation chamber where a high voltage electrostatic field is generated, and the positively charged carbon particles are diverted from the mineral ash particles towards the negative plate. At the

chamber outlet, two plates are put in place to split the diverted particle flows into three product streams: a carbon-rich stream, a carbon-lean stream and the last stream similar to the feed fly ash. Those products are collected using a vacuum conveyance method. A cyclone or bag-filter is usually used to capture very fine refuse ash particles.

To commercialise this design, Tribo Flow Separations, Solvera Particulate/Stock Equipment Company and Boral Materials Technologies collaborated on a demonstration project at the Jack Mcdonough Plant in Georgia in the USA (Lockert and others, 2001). A separator module with a rated throughput greater than $1.1 \times 10^5 \text{ kg/m}^3\cdot\text{h}$ was developed. At a feed rate of 907 kg/h, this separator model ran continuously for four months. The cost of electricity was estimated to be 0.77 \$/t of processed ash, and the total estimated operational cost was approximately 3.3 \$/t (Stencel and others, 1999; Lockert and others, 2001). This module was subsequently developed into the commercial TEP™ module currently available from Tribo Flow Separations. The TEP™ module performance is found to be dependent upon the surface properties and chemical composition of the fly ash. For example, an ash with high surface moisture content tends to have a low degree of separation on the TEP™ module, probably due to the increased aggregation of the ash particles. It is not possible to improve the separation efficiency of a difficult ash by adding an easy-to-separate ash. This is because no synergistic interactions occur between fly ashes with different properties in the TEP™ module (Jiang and Stencel, 2001).

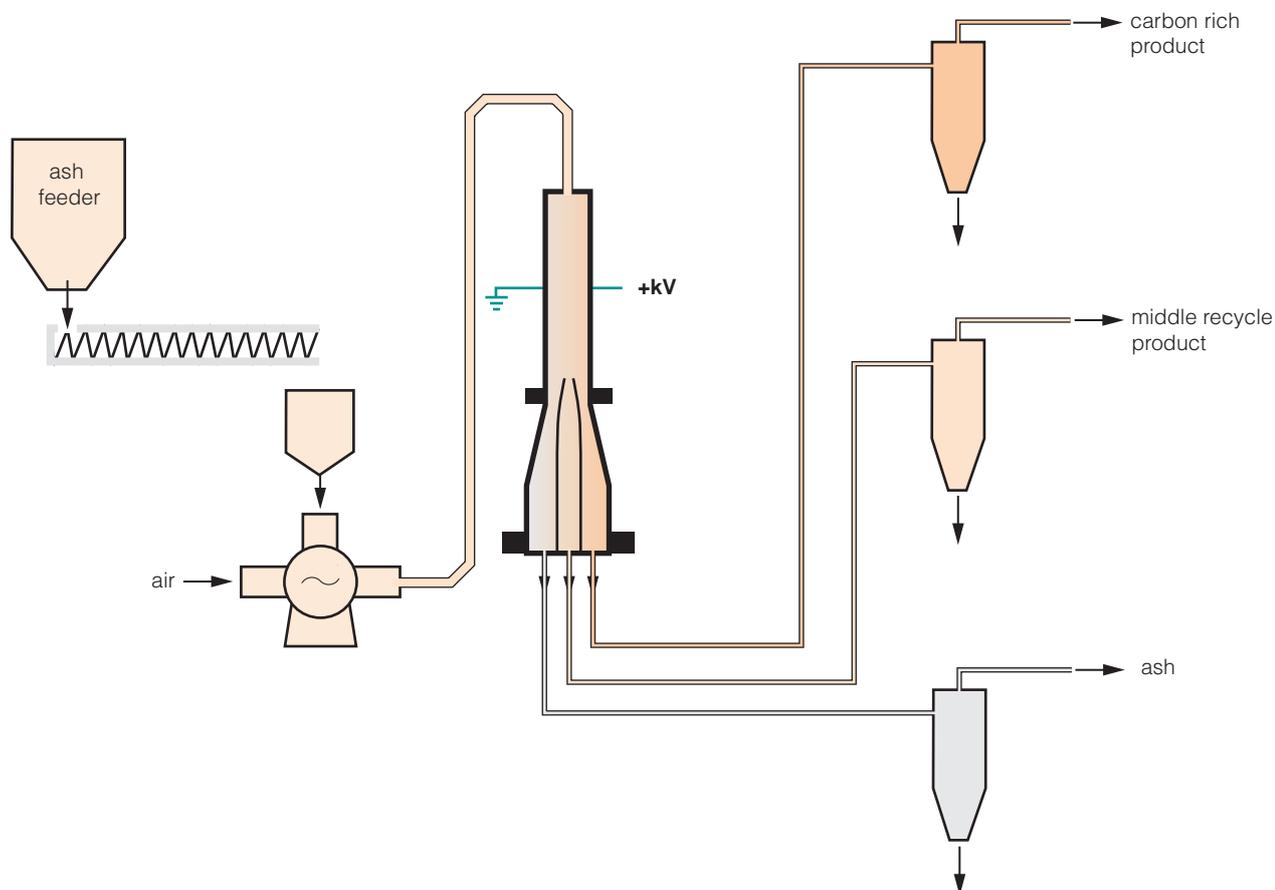


Figure 16 The Tribo Flow Separation process (Lockert and others, 2001)

upstream of the boiler steam turbine. Since the quantity of steam available to drive the steam turbine generator increases, CBO™ improves the overall energy efficiency of a power plant. Taking the Wateree Station in South Carolina for example, its CBO™ plant materially increased its boiler heat rate, reducing coal consumption by about 17 kt/y (Smith, 2005). The exhaust gas from the CBO™ process can be integrated to the main flue gas of the power plant for clean-up, so no additional environmental permits are required. A start-up fuel is still required to increase the furnace temperature to allow auto-ignition of the unburnt carbon (approximately 460°C). Once that auto-ignition has been firmly established, the start-up fuel can be gradually taken off and no additional fuels are required. In practice, the furnace temperature can be easily controlled by recycling some cold product ash back to the furnace. This temperature control method has an additional benefit that minor variations in the LOI of product ash can be smoothed out. If additional temperature control is required, some exhaust gas can be recycled back to the furnace. The entire CBO™ system is maintained at a slightly negative pressure using an induced draft fan.

CBO™ is currently in commercial operation at Wateree Station of South Carolina Electric and Gas (in service since January 1999), Winyah Station of Santee Cooper (in service since September 2002), Brayton Point Station of Dominion Energy and Chesapeake Energy Centre of Dominion Virginia Power (both in service since 2006) (PMI, 2009a). In total, this system now processes in excess of 1 Mt of fly ash annually (Cooper, 2007). Recently, PMI has been awarded 137,884 Greenhouse Gas (GHG) Credits for fly ash processed and recycled in the CBO™ facility at the Chesapeake Energy Centre (PMI, 2009b). This process can accommodate a wide range of LOI values. In the Wateree Station CBO™ facility, fly ash with LOI of 6.5–18% have been processed and the product ash had a consistent LOI value of 2.5% or less (Keppeler, 2001). However, experiences gained from installed facilities point out that blending raw fly ash is necessary to rule out the LOI variation in feedstock. The processed product ash is finer than the raw ash, and is less reactive to adsorb AEA, probably due to preferential burnout of porous char than graphite/soot present in the raw fly ash. Extensive concrete testing has demonstrated the superior pozzolanic characteristics of the product ash (determined as Class F) which is regarded as a premium product for concrete production.

CBO™ is also capable of simultaneously removing ammonia from fly ash. Increasingly stringent NO_x emissions limits have forced boiler operators to use selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) in addition to low NO_x combustion techniques. Both SCR and SNCR use ammonia as the NO_x adsorbent, which will inevitably slip into the fly ash. Fly ash with an excessive amount of ammonia is unmarketable, because it emits an unpleasant odour and is hazardous to workers' health. Nevertheless, ammonia is not detrimental to the structural quality of concrete products. After having investigated the fate of ammonia in a pilot-scale facility under conditions simulating those in commercial scale CBO™ furnaces, PMI concluded that virtually all ammonia (94–98%) contained in

Table 15 The ammonia concentration in feed ash and processed ash (Giampa, 2003)

Ammonia concentration, ppm		NO _x emission reduction system	NO _x emission reduction reagent
Feed ash	Processed ash		
60	<5	SCR	Ammonia
230	<5	SNCR	Ammonia
300	<5	SNCR	Ammonia
500	<5	SNCR	Ammonia
650	<5	SNCR	Ammonia
700	<5	SNCR	Urea
735	<5	SNCR	Urea

fly ash would be thermally decomposed, as shown in Table 15 (Giampa, 2003). Gas measurements made at the furnace exit and exhaust stack confirmed that very little ammonia remained in the exhaust gas.

Mercury is another pollution concern with fly ash. Mercury naturally occurs in coal, and is widely known to pose a high risk to the environment and human health (Sloss, 2002). Mercury may be adsorbed on to fly ash by the unburnt carbon and/or activated carbon deliberately injected for mercury control. It is clear that the adsorbed mercury will vaporise in the CBO™ furnace where the bed temperature (typically 705°C) is much higher than the normal boiling point of mercury (375°C). However, it is unclear whether the vaporised mercury will remain in the gas-phase or recondense onto the process fly ash after the exhaust gas is cooled. To this end, PMI carried out an investigation on a commercial CBO™ facility, which measured the mercury concentration along the exhaust gas flow and the solid fly ash flow (Giampa, 2003). It was found that mercury did volatilise in the bed and the bed material was essentially free of mercury. The vapour phase mercury was entrained along with the low-carbon ash by the exhaust gas into the gas/product cooler. As the temperature of the low-carbon ash and exhaust gas dropped quickly from about 600°C to 150°C, mercury condensed and was subsequently bound onto the product ash particles. The exhaust gas exiting the CBO™ facility therefore contains little mercury. The results showed an excellent mercury mass balance recovery in the range of –6% to +9%.

Microwave Carbon Burnout

Dominion Ash, a Canadian ash marketer, provides a fluidised-bed based combustion process that uses microwave energy rather than start-up fuel to initiate the combustion of the unburnt carbon (Tranquilla and MacLean, 2001). Unburnt carbon is a good microwave receptor due to the very high receptivity of elemental carbon, even in less than 1% concentration. When the unburnt carbon content of fly ash (>7–9% dependent on reactor design) is sufficient to support auto-thermal operation, the microwave energy serves to initiate and throttle the combustion. The combustion is

throttled by adjusting both the excess air ratio and the microwave intensity. If the unburnt carbon content drops, the microwave energy serves to make up the energy input to maintain stable combustion in the furnace. As such, this microwave carbon burnout (MCB) process is capable of accommodating a wide range of LOI values. For instance, fly ash with LOI ranging from 4% to 30% has been successfully processed in the USA and Canada; and the processed fly ash had a consistent LOI value of $\pm 0.5\%$, regardless of the input LOI (Tranquilla and MacLean, 2001).

Similar to the CBO™ process, the MCB process is also capable of removing almost all ammonia from the raw fly ash (Tranquilla and MacLean, 2001). However the MCB process generates NO_x, even when unammoniated fly ash are processed; the NO_x concentration was found to be 200–300 ppm for an unammoniated fly ash with a LOI of 10.8% (Tranquilla and MacLean, 2001). This is surprising because the typical bed temperature of MCB furnaces (approximately 800°C) is much lower than the temperature threshold (>1300°C) at which thermal NO_x formation becomes significant. NO_x generation appeared to be related to the input LOI, but not to be proportional to the actual amount of carbon burned. Since no trace amount of nitrogen was found in the unammoniated ash in the chemical analyses, fuel-N formation was unlikely to occur. The NO_x generation mechanism of MCB process is still unclear.

The fate of mercury in the MCB process is similar to that in the CBO™ process. Virtually all mercury contained in the raw fly ash ends up in the product fly ash. Dominion Ash also developed a microwave pyrolysis process called Mercury Containment specifically for removing mercury from sorbents such as activated carbon and recycling the ‘reactivated’ sorbents. Mercury removed is concentrated into a small volume for containment. Arsenic, another heavy metal of concern, also remains in a thermally stable form in the process ash. Both arsenic and mercury compounds are unlikely to be liberated into water or air and to pose risks to the surroundings once being incorporated into concrete.

5.4.2 Fusion

An ash fusing process has been developed in Japan to turn powdery fly ash into slag which can be used as concrete aggregates (Ishiga and others, 2003). The context behind this process development was that cement demand (and therefore production) dwindled in recent years in Japan, while coal ash production increased due to increased power demand. Consequently, the use of fly ash in cement manufacturing in Japan did not increase. Meanwhile, the natural gravel supply became increasingly scarce in Japan. This fusing process was therefore well suited to Japan’s cement industry.

The concept of the coal ash fusing system proposed by Ishiga is shown schematically in Figure 18. Unlike a cyclone furnace or a slag-tap boiler, this system operates independently of the pulverised coal fired boiler. The fusing furnace is a cylindrical chamber operating at atmospheric pressure. Fly ash collected in the ESP is fed directly from the bottom to the furnace and the coal is fed at a slightly higher elevation. The secondary combustion air is fed tangentially through ports over the coal feed port and creates a downward swirling flow in the furnace. Coal and fly ash are carried by the downward flow to the bottom of the furnace, where coal combustion heat raises the temperature above 1500°C and thus fuses the ash to form a fluid slag. The liquid slag flows down through the slag-tapping hole and is quenched in water. The rapidly cooled solid slag is collected subsequently with a conveyor. A propane burner was used to maintain the temperature in that region at about 200°C higher than the slag temperature to avoid blocking the tapping hole and adhering on the wall underneath the tapping hole. More than 85% of the feed fly ash can end up as slag. The unburnt carbon contained in the feed fly ash is burned out during coal combustion, and the slag has less than 5% unburnt carbon. High-carbon fly ash is preferable in this fusing process.

The product slag provides both environmental and technical benefits. Leaching tests showed that concentrations of

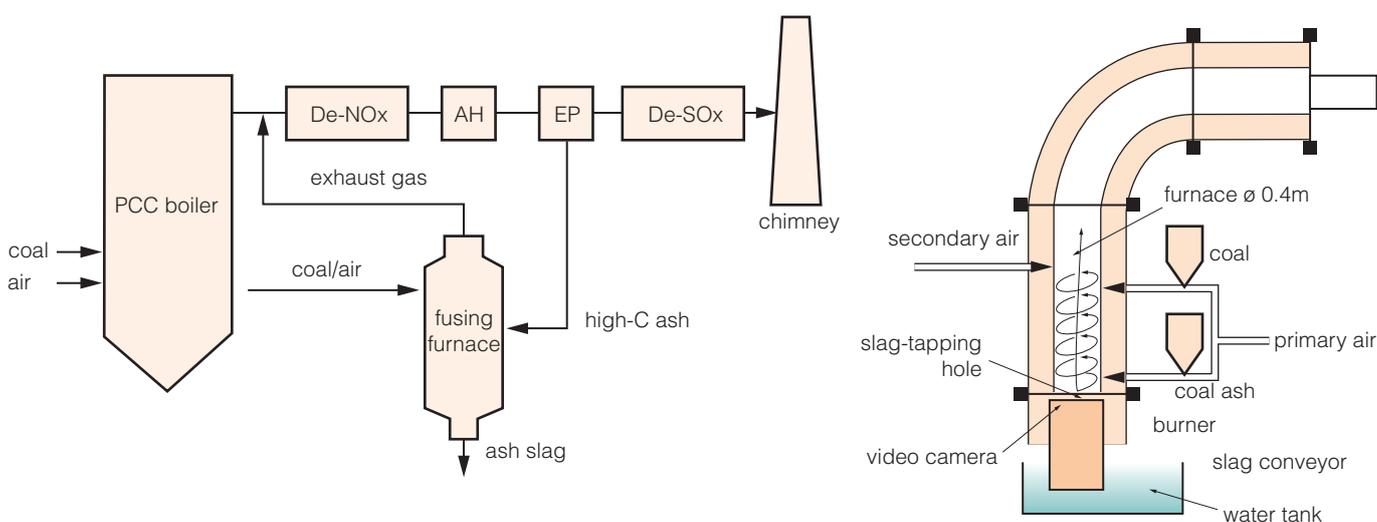


Figure 18 The location of the coal ash fusing system in a PCC power plant and a schematic diagram of the coal ash fusing furnace (Ishiga and others, 2003)

leachable hazardous elements such as selenium, fluorine and chromium present in the run-of-station fly ash may be much higher than permitted in Japanese soil environmental standards. These hazardous elements become less leachable in the fused slag, so using the slag has a much smaller environmental footprint than using the fly ash. Moreover, concrete tests have shown that the fused slag is also less prone to the alkali aggregates reactions (Ishiga and others, 2003). However, the fly ash fusing process generates 10% more NO_x than that generated from coal combustion alone. Nevertheless, the overall NO_x concentration is no more than 150 ppm, so still comparable to that of typical PCC boiler flue gas (Ishiga and others, 2003). Combining the exhaust gas from the fusing furnace to the main flue gas stream of the boiler still allows the operators to meet their plant environmental control targets.

Ishikawa (2005), a co-investigator of the above-mentioned coal ash fusing system, proposed another fly ash fusing process for the production of inorganic fibres. The major

difference of this process for the above-mentioned process is that the cylindrical fusing furnace is replaced by a circulating flow combustor (*see* Figure 19), which uses low-cost coals to reduce the fuel cost. An important feature of the combustor is that coal, fly ash and combustion air are all circulating in the lower part of the combustor. Such circulation provides sufficient residence times for coal/unburnt carbon combustion and ash fusion in the furnace. Moreover, the fused ash particles (liquid slag) are thrown out of the combustion zone by the centrifugal force created by the circulation towards the wall and flow down to the combustor bottom for discharging. As such, the direct collision of liquid slag with ascending air flows is reduced and a more stable slag discharge can be maintained. Flux materials, such as CaCO₃, are normally added into the furnace to lower the fusion point of coal ashes. Part of the liquid slag is used in fibre-making equipment; and the remaining is recovered as solid slag for uses such as fine concrete aggregate or a road base material.

The fibres produced in Ishikawa's experiments were claimed

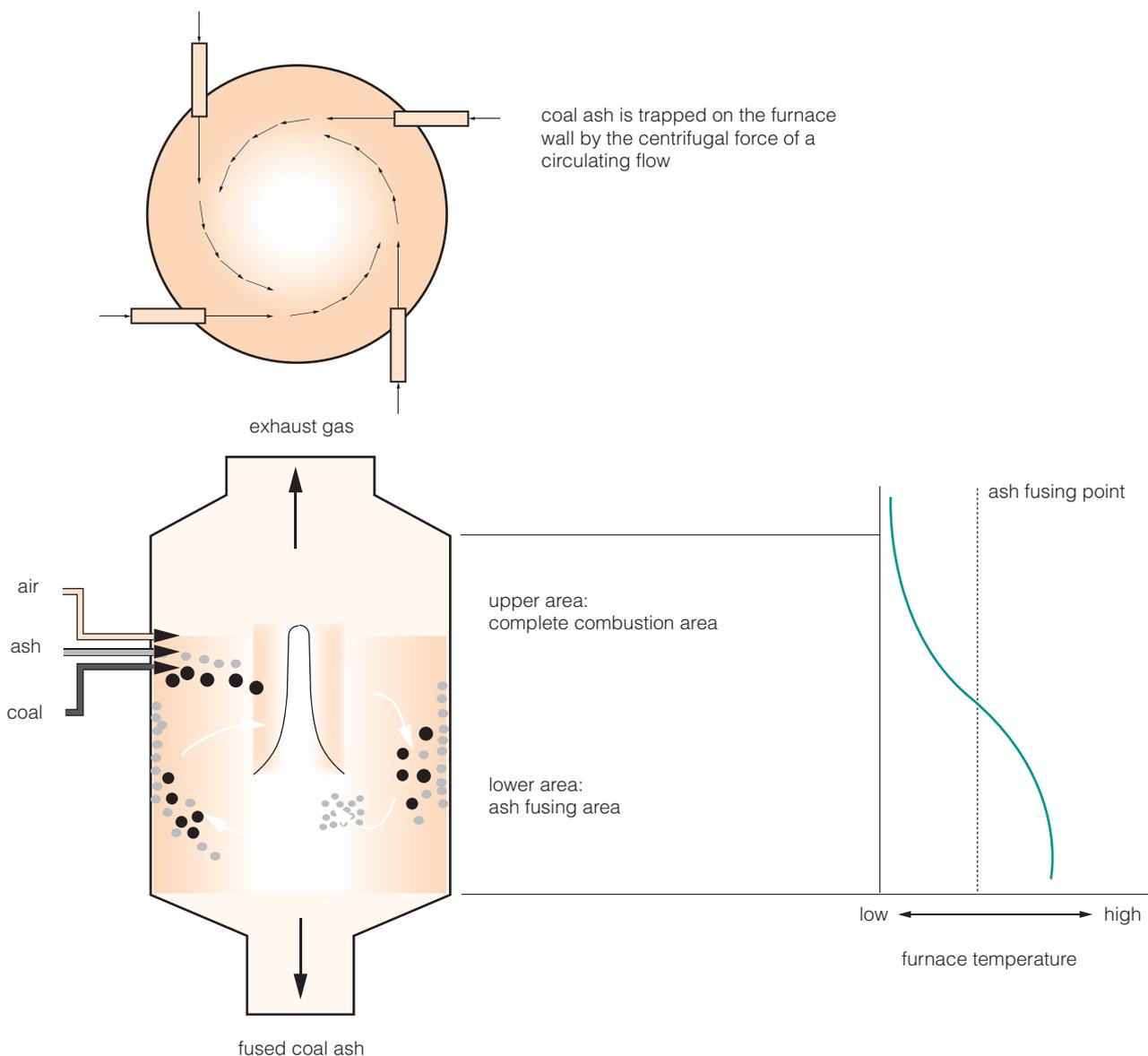


Figure 19 A circular combustion type coal ash fusing furnace (Ishikawa, 2005)

to have a better quality than other inorganic fibres such as rock wool. The slag fibre showed good thermal resistance. When heated up to red-heat and then quenched in water, the fibre did not break or show a condensation colour, nor lose its softness. The application temperature of the coal ash fused fibre was better below 1050°C. However, if the application time was short, fibres could also withstand temperatures up to its melting point, just like ceramic fibres. The weight loss on ignition was very low, 0.2 wt%, indicating a complete burnout of the feed coal as well as the residual carbon in the feed coal ash. The excellent properties of the fly ash-based slag fibre make it suitable for a wide range of applications encompassing heat insulation, sound absorbing, a refractory material and a concrete strengthening material. The inorganic short fibre market size in Japan was more than 500,000 t in 2001 (Ishikawa, 2005). Asbestos, a well-known carcinogenic material, accounted for approximately 16% of the market in 2001. If the slag fibre substitutes for all asbestos, not only would human health be better protected by the avoidance of contact with asbestos, but also fly ash utilisation could be further expanded in Japan. Given the comparable price to that of asbestos, the sales of the slag fibre can bring in additional revenue up to billions yen/year to the fly ash marketers (Ishikawa, 2005). The slag fibre has the potential to be economically competitive with rock wool and glass wool in the present inorganic short fibre market in Japan.

5.4.3 Steam gasification

A gasification process using supercritical water to remove the unburnt carbon in fly ash has been proposed by researchers from the University of Nottingham in the UK (Hamley and others, 2001). The supercritical steam can react intensively with carbon due to the elevated temperature and pressure. In addition, the supercritical steam is also capable of rapidly destroying the organic compounds and toxic wastes. In the laboratory tests conducted in the University of Nottingham, fly ash produced from seven different coals have been treated by steam generated from a 2% solution of hydrogen peroxide, which decomposed at high temperature to provide excessive oxidant. Results showed that the LOI value decreased for all the ash samples after the gasification treatment; a larger reduction occurred for fly ash that had larger LOI values. For instance, a Colombian coal ash with LOI of 20.78% achieved a reduction to just 3.62% (LOI), or by 82.5%. In contrast, the process reduced the LOI of a Russian coal ash from 4.37% to just 3.54%. The higher reactivity of unburnt carbon in fly ash from South American coals, such as the Colombian coal, might be part of the reason.

Researchers at the University of Nottingham argued that this process is capable of removing unburnt carbon more reliably and completely than other alternative methods, given the higher temperature and pressure used in this steam gasification process. However, acid corrosion as a result of the oxidation of chlorine, sulphur and phosphorus present in the fly ash causes safety concerns. At the high operating temperatures, corrosion caused by those acids can be very intensive. Fouling of inorganic salts is another major concern. Under the high temperatures, these inorganic salts may vaporise and subsequently condense onto cold surfaces.

Again, the researchers argued that neither the acids or inorganic salts exist in sufficient quantities to cause the above-mentioned problems. Nevertheless, accumulation of these detrimental substances present potential operating risks.

5.5 Carbon surface modification

Rather than burning off the residual carbon in the fly ash, modifying the surface chemistry of the residual carbon may also render the carbon less effective in adsorption of AEA. Hachmann and others (1998) have observed that fly ash's adsorption of AEA could be considerably weakened by exposing the fly ash to air at 350–450°C (but no measurable combustion occurred). In contrast, if the fly ash was exposed to inert gases at 900°C or above, its adsorption of AEA increased because the pre-existing oxides had been driven off. Gao and others (1997) also reported that oxidation treatment of the surface of carbon black samples rendered them less adsorptive than the untreated samples. These observations seem to suggest that oxide-free carbon surfaces are more reactive with AEA surfactants. The reason may be that the oxide-free carbon surface is non-polar (hydrophobic) so as to compete with air bubbles for the hydrophobic ends of the AEA molecules. Intentional oxidation of the carbon surfaces can therefore effectively suppress the adverse effect of unburnt carbon on air entrainment in concrete production.

Surface oxidation treatment is particularly attractive when the unburnt carbon content is relatively low, so that thermal processes such as CBO™ cannot operate continuously without the addition of complementary fuels or energy. Since the surface oxidation operates at much lower temperatures compared to thermal processes, powerful oxidants, ozone for example, are normally used. Hurt and others (2003) patented an ozone treatment process and their laboratory tests demonstrated the effectiveness and the potential for commercial application of this technique (Chen and others, 2001). A fixed bed reactor was used in their study, where an air stream with 500 ppm – 2 vol% ozone passed through the ash bed for a prescribed contact time (1 min – 20 h). Results showed that all ozonated samples have reduced AEA adsorptivities; an ozone dosage rate in the range of 0.5–3 g/kg of fly ash is required to achieve the desired effect of ash adsorptivity reduction (Hurt and others, 2003). Sharp reductions in adsorptivity were observed when about 3 g O₃/kg ash had been charged into the ash bed. Addition of more ozone into the ash bed did not result in a further significant reduction. Class C ashes were found to require more O₃ per unit of carbon to achieve the same effect as observed for Class F ashes. This trend was consistent with the higher specific surface adsorptivity of carbon in most class C ashes (Külaots and others, 2002). The reduction in fly ash's AEA adsorptivity was found to continue during ash storage in bottles under ambient conditions for up to nine months.

The mechanism of this reduction in AEA adsorptivity was revealed by surface energy analyses and X-ray photoelectron spectroscopy analyses. Polar oxygen functional groups, such as C-O, C=O, and O-C=O increased on the carbon surfaces after the ozonation. Furthermore, exposing ozonated ash samples to 1000°C in helium for 10 min was found to restore

most of their initial adsorptivities (Chen and others, 2001). The amount of ozone required to achieve a given adsorptivity reduction was directly proportional to the total surface area of carbon determined by the N_2 -BET technique. It was also found that the major reduction in adsorptivity occurred when a monolayer of oxides had been formed on the carbon surface. However, the maximum reduction corresponded to formation of more than one layer of oxides. This indicates either excessive ozone uptake into the thick ash bed with no additional oxidation actually taking place, or other reaction pathways for ozone, which need further investigation.

The economics of this ozone treatment technique were also briefly discussed by Chen and others (2001). The primary cost is for electricity used for ozone generation, estimated from equipment vendor data at about 15 kWh/kg ozone. Given the electricity cost in 1999 and an ozone usage of 1–2 g O_3 per kg ash, the electricity cost for ash treatment was estimated to be 0.3–1.3 \$/t ash. Compared to the potential revenues from marketing the resulting saleable ash, the cost is acceptable. More economic benefits arise if avoided ash disposal cost is considered. The authors therefore regarded this ozone treatment technique as a promising commercial alternative to physical carbon separation or carbon burnout processes. Efforts have been made to further understand the detailed kinetics and mechanism of the ozonation process. A pilot-scale demonstration project has been conducted successfully at a power station of Pennsylvania Power and Light (PPL). Participants include the US DOE, PCI-Wedeco Environmental Technologies Inc in New Jersey and the Electric Power Research Institute (Hurt, 2009).

Nevertheless, ozone generation is still the inherent cause of the relatively high operating cost of this process. The overall power consumption associated with ozone generation is estimated to be in the range 9–18 kWh/kg (FreshPatents, 2009). The average ozone dosage of 0.5–3 g per kg of fly ash is also relatively large. Ozone treatment is therefore an expensive approach to address the carbon-in-ash issue. Furthermore, since ozone is toxic, any excess has to be broken down into atmospheric oxygen. Ozone therefore requires careful management, including dosage rate adjustment, optimum ozone-ash contacting, and a back-up breakdown system which is based on catalysts such as manganese dioxide or thermal treatment at 300°C. Finally, since the carbon remains in the fly ash, unexpected problems may occur over the long term once the fly ash is incorporated in concrete products. This is possible since the ozonation mechanism is still not fully understood.

Carbon surface treatment can also be realised using chemical injection or spray methods. The chemicals widely used include aliphatic or aromatic carboxylic acids and their salts. These chemicals are ‘air-neutral’, neither promoting nor retarding the performance of air entrainment agents. A commercial example is the proprietary formula of chemicals used in the FACT™ (Fly Ash Carbon Treatment) process developed by Boral Material Technologies Inc, which has been successfully demonstrated with more than 2.7 Mt of fly ash (Hill and others, 2009). The FACT™ admixture is highly reactive with carbon, but has little impact on air entrainment or cement hydration properties. It is sprayed into the flowing

ash stream when the fly ash is being loaded into the transport truck for delivery. The standard dosage rate is often based on the worst-case-carbon scenario for a particular plant, which hence provides a safety warranty against any unexpected variations in the carbon-in-ash.

However, it is often difficult to achieve homogeneous distribution of the spray due to the high mass flow rate of fly ash. Penetration of the admixture into the centre of the flowing ash stream may be poor. In some cases, overspill of the admixture is potentially hazardous to the environment or workers’ health (Boggs, 2003). Similar to ozone, the admixture does not remove carbon from the fly ash, so there may be unpredictable consequences once the treated fly ash is used in concrete production. Wet treatment, with ammonium persulphate and acetic acid for example, may incur high drying costs and potential problems with self-cementation or loss of pozzolanic reactivity.

Another noteworthy issue is the preferential adsorption of the treatment chemicals by activated carbon. Anticipating restrictions on mercury emissions, more utilities are facilitating mercury capture from the boiler flue gas. The most widely used means is the injection of a powdered activated carbon into the flue gas stream. Inevitably, the fly ash would be contaminated with a small amount (typically 3%) of powdered activated carbon. Due to its high adsorptive capacity, activated carbon is more reactive with treatment chemicals than unburnt carbon in the fly ash. For example, it has been found that the FACT™ admixture only works for fly ash with less than 1% powdered activated carbon (Hill and others, 2009). To overcome this issue, Hill and others (2009) developed a new formula of the treatment admixture that has proved effective for fly ashes with >3% activated carbon. In addition, the variation in the air content of the resulting concrete was also reduced from 9% to less than 3% for fly ash with 0–3% activated carbon. Further investigation is under way to validate the effect of this formula on the freeze-thaw performance of concrete for its full commercial application.

5.6 Summary

This chapter introduces briefly various methods for reduction of unburnt carbon in fly ash. Classification is the most widely used method, based on the fact that the majority of unburnt carbon concentrates on large particles. But that also means this method would fail for very fine carbon particles. Froth flotation exploits the hydrophobicity of unburnt carbon in fly ash. However, it is difficult to float intensively oxidised carbon without the addition of flotation collectors. Frothers can be used to reduce the dosage of flotation collectors. Triboelectrostatic separation is based on the principle that mineral ash particles and carbon particles will take on opposite charges in an electric field. This chemical-free and compact method is efficient and reliable with a long record of commercial success. In addition to the saleable fly ash, the unburnt carbon can be recovered as a solid fuel. Thermal processes recover the thermal energy from unburnt carbon through combustion, fusion or steam gasification. It is important that the process operates without consumption of complementary fuel. Carbon surface modification is often

considered for fly ashes with relatively low unburnt carbon content, because the other carbon reduction methods are not economically viable for these fly ashes. This method is however expensive due to the use of costly chemicals and measures to prevent their release into the environment. The resulting product ash may also suffer from low consistency in its quality.

6 Pollution concerns

As discussed briefly in Section 5.4, ammonia and mercury present in the fly ash are a concern because of their potential hazard to the environment and human health. The saleability of fly ash may therefore be impaired. This section discusses in more detail their environmental impact and methods to remove them if necessary.

6.1 Ammonia

Ammonia compounds, primarily sulphates and bisulphates, in the fly ash are derived from ammonia injected for NO_x emissions control in SCR/SNCR or for improvement of ESP performance. Ammonia slip is inevitable in practical operation and even a few ppm slip in the gas phase may result in a few hundreds of ppm ammonia in the fly ash, because the mass of fly ash is about two orders of magnitude smaller than the flue gas (Bittner and others, 2001). During concrete production, the ammonium ions in solution are converted to molecular ammonia due to the alkalinity of the concrete mix ($\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$). Although the ammonia concentration is usually less than 100 mg NH₃/kg fly ash, elevated concentrations may be encountered if the SCR catalysts become aged or problems occur with the ammonia injection system. Since ammonia is volatile and has an unpleasant odour, a fly ash becomes unacceptable for use if its ammonia concentration exceeds 200 ppm or even at a lower level with poor ventilation, even though ammonia does not have an adverse impact its pozzolanic properties (Bittner and others, 2001).

It is thus necessary to reduce the excessive ammonia concentration in fly ash in order to render it saleable. There are commercially available processes for ammonia removal from fly ash, which can be broadly categorised into thermal and chemical processes. Thermal processes operate either at temperatures higher than the decomposition temperature (typically 434°C) of primary ammonia species or at temperatures (150–260°C) sufficient for ammonia desorption from fly ash (Groppo and others, 2004). The CBO™ and MCB processes described in Section 5.4.1 can be regarded as examples of the former thermal process. Given the high operating bed temperatures of CBO™ (at about 705°C) and MCB (between 650°C and 850°C), ammonia species in the fly ash can be effectively decomposed. Examples of the thermal desorption process include the ASH PRO™ Liberation Process (Fisher and Blackstock, 1997) and the inclined bubbling fluidised bed system with acoustic enhancement (Levy, 2002; Levy and Lawton, 2003).

Chemical processes, such as Separation Technologies' lime-slaking ammonia removal process, use alkali chemicals to shift the ammonium ion-molecular ammonia equilibrium towards the volatile ammonia ($\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$) so that ammonia compounds in fly ash can be reduced. A key feature of the ST ammonia removal process is the use of a minimum quantity of water (1–4%) and minimal quantities of alkali (<2%). A large quantity of water is detrimental, not

only slowing the rate of ammonia release but also causing self-cementing or reducing the pozzolanicity of fly ash in some cases. Typically, less than 1% Ca(OH)₂ is sufficient to achieve the pH (>10) required to shift the equilibrium, even for fly ash which is naturally acidic (Bittner and others, 2001). Excessive alkali does not aid ammonia release if insufficient water is present and vice versa. Calcium-based alkalis also result in minimal alteration of the fly ash chemistry. Separation Technologies' ammonia removal process can be used alone or in combination with the company's triboelectrostatic carbon separation technology. The triboelectrostatic carbon separation process is not affected by the presence of ammonia. This modular approach offers the lowest cost solution for treating otherwise unusable fly ash. Three full-scale lime-slaking ammonia removal facilities are now in operation at the St John's River Power Park (USA), the Big Bend Station of Tampa Electric Company (USA), and RWE npower's Aberthaw ash processing facility in the UK (Bittner and Gasiorowski, 2003; Bittner and others, 2009). At the Big Bend Station, the ammonia removal facility is integrated into the triboelectrostatic carbon separation process provided by Separation Technologies. Ammonia concentrations of less than 100 ppm have been reliably achieved in the processed fly ash.

A Utah-based American company, Headwaters Resources Inc, is marketing an ammonia reduction process that uses hypochlorites. Hypochlorites can partially or completely oxidise ammonia to monochloramine and chloride salts, which at low concentrations are harmless to concrete products. Monochloramine does not dissipate into the air, therefore, eliminating the unpleasant odour of ammonia. Moreover, the oxidation treatment seems to have a positive effect on the concrete quality such as compressive strength. The reagents can be added and blended with the dry fly ash at any point between the fly ash collection system at the power plant and final delivery to the ready mixed concrete producer (Headwaters Resources, 2009).

6.2 Mercury

In response to more stringent regulations on mercury emission, coal-fired power plant operators have applied the activated carbon injection method to capture mercury from flue gas. Since captured mercury is collected along with fly ash and FGD products, there are concerns about possible mercury release from CCP over their long-term applications. The current level of fly ash utilisation may be undermined by such concerns. The US DOE estimated a loss of 908 million \$/y for fly ash and a loss of 213 million \$/y for FGD products reuse applications (Buckley and Pflughoeft-Hassett, 2007). The potential environmental impact of mercury release from CCP has therefore become an attractive field for research over the past decade. Three release mechanisms for mercury from CCP have been identified: leaching, vapour-phase release and biologically induced release (Hassett and others, 2005). Leaching is the most likely

mechanism of mercury release from CCP with the presence of water. Vapour-phase release of mercury is important from the perspective of long-term use, storage or disposal of CCP. Biologically induced leaching and vaporisation are also of great concern because mercury can be converted by bacteria to methylmercury, which is particularly toxic to the brains of human beings and animals.

The University of North Dakota Energy & Environmental Research Center has made an in-depth four-year investigation on the potential of mercury and other air toxic elements releases from CCP (Buckley and Pflughoeft-Hassett, 2007). Direct leaching tests conducted indicated that mercury was not readily leached from fly ash or FGD materials. Leachate concentrations were below the 0.01 µg/L analytical reporting limit for most samples evaluated. Laboratory tests indicated that significant vapour-phase mercury release from CCP is unlikely at ambient-temperature. Mercury vapour-release was low at temperatures lower than 250°C, and 100% of the mercury release from CCP only occurred at above 750°C. Under microbiologically mediated conditions, only very low levels of elemental and organomercury were released in the vapour-phase and leachate. Field experiments conducted at a lignite CCP disposal site also suggested low vapour-phase mercury release from lignite fly ashes but noticeable release from FGD product materials. More investigations are continuing on the potential for mercury release under a variety of management situations. Nevertheless, research conclusions to date indicate that mercury present in CCP has a low possibility of release under most management conditions (Buckley and Pflughoeft-Hassett, 2007). However, at temperatures above 411°C, mercury and its oxides can be released from CCP in considerable quantity (Hassett and others, 2005).

Long and others (2009) conducted a risk assessment study of the possibility of mercury release into indoor air from fly ash concrete blocks and FGD gypsum wallboard. Results showed that indoor atmospheric mercury concentrations were generally consistent with, or below, ambient background mercury levels, even though the exposure to mercury is overstated. Moreover, the estimated indoor atmospheric mercury concentrations were well below permitted inhalation toxicity criteria. The authors thus concluded that CCP-contained construction materials are unlikely to pose mercury-related threats to human health in public buildings or residential homes.

Although mercury is unlikely to release once it is bound onto fly ash, other concerns have been raised with respect to activated carbon capturing other metals, for example arsenic, which can easily leach out of fly ash. These concerns are still under review, without final conclusions. Moreover, activated carbon can also deactivate the AEA. Sorbent Technologies developed a new mercury sorbent, C-PAC™, that is claimed to be inert to the AEA. Such a concrete-friendly sorbent is a gas-phase brominated powdery activated carbon manufactured in a patented proprietary process. Tests conducted at the Power Station of Midwest Generation LLC successfully demonstrated its capability of achieving an average 81% removal of gas-phase mercury as well as maintaining the fly ash suitable for use in concrete production

(Zhou and others, 2007). The specific foam index (SFI) of C-PAC™ was only a fraction of that of unburnt carbon in the ash. It was also found that C-PAC™ did not affect the setting of the concrete but increased the early concrete strength by 10–15% compared to the concrete incorporating sorbent-free fly ash. In two recent full-scale trials at the Corette Steam Generation Station of PPL Montana and at the Waukegan Station of Midwest Generation in Illinois in the USA, C-PAC™ injection at 48.1 mg/m³ was sufficient to meet the pending US mercury reduction standard (80% reduction) (Lipscomb and others, 2009). Fly ash produced from the Corette Station was sold by an ash marketer, Headwaters Resources, to the concrete industry. Experiences at the Waukegan Station showed the C-PAC™ sorbent still performed well at elevated temperatures in the hot-side ESP.

6.3 Summary

This chapter discusses the pollution concern about fly ash, primarily due to its ammonia and mercury contamination. Ammonia at excessive concentrations may impair the salability of fly ash due to its unpleasant odour and potential hazard to workers' health. There are thermal and chemical processes available to remove the ammonia from fly ash. It has been found that virtually all mercury is retained on the processed fly ash during thermal processes. Scientific research findings to date indicate that mercury is unlikely to release into the environment in leachate or vapour under most management or utilisation conditions. A 'concrete-friendly' mercury sorbent C-PAC™ is now commercially available to reduce the impact of activated carbon, the conventional mercury sorbent, on the air entrainment of concrete. However, other metals captured along with mercury by activated carbon, for example arsenic, still cause concerns about the use of fly ash in construction applications.

7 Conclusions

Coal fly ash production is expected to increase as a result of the world's increasing reliance on coal-fired power generation over the next few decades. Dealing with such a large waste stream is becoming an important environmental issue. The conventional landfill approach is constrained by concerns over the potential for underground water pollution and rising costs of obtaining land and disposal site management. This concern has recently increased in the USA following the unprecedented fly ash spill from the Kingston Fossil Plant in Tennessee. Consequently, almost all major coal-consuming countries are promoting beneficial utilisation of fly ash. The largest-volume and most profitable utilisation option for fly ash is as a cement raw material or replacement for clinker in cement manufacture and replacement for ordinary Portland cement in concrete production.

However, fly ash use in cement/concrete is undermined by the carbon-in-ash issue, in that excessive unburnt carbon in fly ash adversely affects the air entrainment performance of concrete. With inadequate air bubbles trapped in the concrete structure, the concrete is vulnerable to freeze-thaw cycles, leading to cracks and weakened mechanical strength. The marketability of the fly ash is therefore reduced.

Excessive unburnt carbon in fly ash is also undesirable from the plant operation perspective. It represents an apparent fuel loss so that the overall plant efficiency is reduced. Moreover, the performance of electrostatic precipitators is degraded by an excessive carbon level because carbon has high conductivity and loses electric charges quickly. As a consequence, the stack opacity may increase considerably, making it difficult to comply with particulate emission regulations.

The immediate response to the carbon-in-ash issue is to improve coal burnout in boiler furnaces. The greatest challenge for present-day boiler operation is to achieve both low NO_x emissions and satisfactory coal burnout. Improving the fineness of coal mill output using a dynamic classifier is the most effective measure to improve coal burnout, which requires coal cleaning and optimisation of coal mills. It is also important to reduce any air/coal distribution imbalance among burners, to increase air-coal mixing rates at both burner and OFA levels, and to increase local oxygen availability and coal particle residence time before reaching the convective pass. A plasma-assisted combustion enhancement can achieve better ignition and a more stable flame for less combustible coals. Finally, computer-based combustion diagnostic tools and optimisation systems are becoming invaluable measures to tackle the carbon-in-ash issue.

In all the national standards for fly ash use in cement/concrete, the permitted concentration range of unburnt carbon in fly ash is indicated by the loss on ignition (LOI) parameter. This mass-based parameter can be measured quickly and serves practically as the first step in fly ash quality control. It is also clear that the absolute quantity of unburnt carbon alone is not sufficient to judge the suitability

of a fly ash for use in cement/concrete production. To determine precisely that suitability, the actual morphological properties of a fly ash need to be taken into account. However, at present only few national regulatory standards, for example the US standards, involve terms for so-called performance-based fly ash specifications for use in concrete applications.

Apart from China and Russia which allow for relatively high LOI values for certain ashes, the other major coal-consuming countries stipulate similar LOI limits for fly ash for use in concrete production. This broad consistency in permitted LOI range is perceived to be beneficial for development and wider deployment of carbon-reduction technologies.

Carbon-reduction technologies are key to the increased and expanded beneficial utilisation of fly ash. There is a variety of methods for carbon reduction from fly ash. As the simplest method, classification works by the fact that the majority of unburnt carbon concentrates on large particles. Froth flotation has been used to recover disposed fly ash into a useful fly ash product and an unburnt carbon-based solid fuel. Triboelectrostatic separators are chemical free, reliable and also compact. Thermal processes can recover the thermal energy from unburnt carbon through combustion, fusion or steam gasification. Carbon surface modification is often considered for fly ashes with relatively low unburnt carbon content, because the other carbon reduction methods are not economically viable for these ashes. Ammonia and mercury contamination are becoming barriers for fly ash utilisation. There are thermal and chemical processes available to remove the ammonia from fly ash. Scientific research findings to date indicate that mercury is unlikely to release into the environment in leachate or vapour under most management or utilisation conditions.

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